HIGH STRAIN CRYSTAL GELS , GEL COMPOSITES
AND ARTIFICIAL MUSCLES

RELATED APPLICATIONS

This application is a continuation-in-part of the following applications: 09/412,886, filed 10/5/99; 09/285809, filed 4/1/9909/274498, filed March 23, 1999; 08/130,545, filed August 8, 1998; 08/984,459, filed 12/3/97; 08/909,487, filed 7/12/97; 08/863,794, filed 5/27/97; PCT/US97/17534, filed 30 September 1997; U.S. Serial No: 08/719,817 filed September 30, 1996, U.S. Serial No: 08/665,343 filed June 17, 1996 which is a Continuation-in-part of U.S. Serial No: 612,586 filed March 8, 1996; PCT/US94/04278 filed 4/19/94 (published 5/26/95 No. WO95/13851); PCT/US94/07314 filed 6/27/94 (published 1/4/96 No. WO 96/00118); 288,690 filed 8/11/94; 581,188 filed 12/29/95; 581,191 filed 12/29/95; 581,125 filed 12/29/95 now U.S. Patent No. 5,962,527. In turn U.S. Serial Nos. 581,188; 581,191; and 581,125 (now US Patent 5,962,572) are continuation-in-parts of the following applications: Serial Nos.: 288,690, filed August 11, 1994, PCT/US94/07314 filed June 27, 1994 (CIP of PCT/US 94/04278, filed 19 April 1994). The subject matter contained in the related applications and patents are specifically incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to novel gels, composites and articles as artificial muscles.

BACKGROUND OF THE INVENTION

There have been many breakthroughs published on the internet including muscles made from flexible polymer ribbons constructed from chains of carbon , fluorine, and oxygen molecules (Yoseph Bar-Cohen @ www.discover.com/augustissue/ breakbend bots.html). Mo Shahinpoor makes his out of polyacrylonitrile, see www. sciam.com/ explorations/050596explorationsbox4.html; and a polymer muscle consists of thin sheets wrapped into a cigarlike cylinder.

Other types of (internet announced) polymer muscle are thin sheets of wrapped into a cigarlike cylinder. These polymers stretch when one side of a sheet is given a positive charge and the other a negative. These charges cause each wrapped sheet to contract toward the center of the cylinder, and this construction forces the cylinder to expand lengthwise. When the power supply is off, the rope relaxes. These polymers can push, pull, and lift loads.

SRI International is investigating artificial muscle for small robots using electrostrictive polymers. The muscle has compliant electrodes on the surface of the polymer film, contracts in thickness and extends in length and width due to the electrostatic forces when a voltage is applied. The polymer enhances the electrostatic force because of its dielectric constant. The net result is a muscle with a large strain (>30%) and a large actuation pressure (0.21 MPa in silicon, 1.9 MPa in polyurethane). The performance of the artificial muscle is comparable to the natural muscle, but with higher efficiency and faster response.

Artificial muscle can be fabricated using spin coating, dipping, or casting. Once the muscle is fabricated, it can also be folded or rolled to make the muscle actuator more compact. The artificial muscle actuator shown in Fig 2 uses a spin coated film which is first folded then rolled, followed by folding and to achieve 20 layers. The active muscle for the actuator is 10 mm in length and 3 mm in diameter, and gives a maximum stroke of 1 mm and maximum force of 2 grams (2 X 10^4uN). Its weight is approximately 0.1 grams.

The ability to reduce the number of layers and increase the muscle material's strain, thereby greatly reducing the size of the active muscle actuator and/or increasing the stroke distance at a greater force are challenges not achieved in the prior art.

This application is based upon subject matters described in earlier filed and copending related applications and patents (see *Related Applications* above) which are specifically incorporated herein by reference.

SUMMARY OF THE INVENTION

I have now discovered novel crystal gels with improved properties made from thermoplastic elastomer random copolymers and block copolymers having one or more substantially crystalline polyethylene segment midblocks exhibiting greater advantage over other non-crystalline component forming gels for making artificial muscles. The crystal gels advantageously exhibit high tear resistances, high tensile strength and exhibit high strain under elongation. Such crystal gels are advantageous for end-use involving repeated applications of stress and strain resulting from large number of cycles of elongations, deformations, including compression, compression-extension (elongation), torsion, torsion-compression, torsion-elongation, tension, tension-compression, tension-torsion, exhibit high strain under elongation and the like. The crystal gels also exhibit improved damage tolerance, crack propagation resistance and especially improved resistance to high stress rupture which combination of properties makes the gels advantageously and surprisingly exceptionally more suitable for use as artificial muscles than amorphous gels made from non-crystalline poly(ethylene) component copolymers at corresponding gel Bloom rigidities.

The artificial muscle actuators of the invention comprises one or more thin film layers folded or rolled into the shape of a cylinder forming a center part of said cylinder and an outer part of said cylinder, said film layer having a top surface and a bottom surface, said top surface and said bottom surface each coated with an electrical conducting layer, said conducting layer of said top surface connected by a first electrode on said top surface positioned at said center part and said bottom surface connected by a second electrode on said bottom surface positioned at said outer part; said first and second electrodes being connected to a direct current power source, said power supply capable of generating a electrical potential of a positive electrical charge to the first electrode and a negative electrical charge to the second electrode of at least about 10,000 volts; said film layers comprising a crystal gel made from one or more copolymers characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 25°C as

determined by DSC curve, and said crystal gel being characterized by sufficient crystallinity as to exhibit a melting endotherm of about 25oC, 21oC, 22oC, 23oC, 24oC, 25oC, 26oC, 27oC, 28oC, 29oC, 30oC, 31oC, 32oC, 33oC, 34oC, 35oC, 36oC, 37oC, 38oC, 39oC, 40oC, 41oC, 42oC, 43oC, 44oC, 45oC, 46oC, 47oC, 48oC, 49oC, 50oC, 51oC, 52oC, 53oC, 54oC, 55oC, 56oC, 57oC, 58oC, 59oC, 60oC or higher as determined by differential scanning calorimeter (DSC) curve, said crystal gel having rigidities of from less than about 2 gram Bloom to about 1,800 gram Bloom; and said crystal gel having sufficient crystallinity so as to exhibit greater strain under elongation than amorphous gels of SEPS and SEBS.

The usefullness of the crystal gels as artificial muscles is because of the inherent crystallinity of one or more components of the copolymers forming the crystal gels which makes the crystal gels useful as artificial muscles. The crystallinity provides greater strain under elongation which advantage is surprisingly not found in gels of corresponding gel rigidities made from amorphous block copolymers such as poly(styrene-ethylene-butylene-styrene), poly(styrene-ethylene-propylene-styrene), high vinyl poly(styrene-ethylene-butylene-styrene), poly(styrene-ethylene-ethylene-butylene-styrene) alone.

As used herein, the term "gel rigidity" in gram Bloom is determined by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square centimeter at 23oC.

The various aspects and advantages will become apparent to those skilled in the art upon consideration of the accompanying disclosure.

DESCRIPTION OF THE DRAWINGS

Figs. 1. Representative sectional view of crystal gel, composite and gel articles useful as artificial muscles.

Figs. 2A -2d. Representative sectional view of crystal gel, composite and gel articles useful as artificial muscles.

Figs. 3A - 3n. Representative sectional view of crystal gel, composite and gel articles useful as artificial muscles.

Figs. 4a.- 4x. Representative sectional view of crystal gel, composite and gel articles useful as artificial muscles.

DESCRIPTION OF THE INVENTION

Thermoplastic elastomer gels are described in my patents and published applications: PCT/US97/17534; PCT/US94/04278; PCT/US94/07314; 5884639; 5868597; 5760117; 5655947; 5624294; 5508334; 5475890; 5336708; 5324222; 5262468; 5239723; 5153254; 4,618,213; and 4,369,284. Various patents on thermoplastic elastomers and blends are described in U.S. Patent Nos. 5,755,243; 3,595,942, Reissue 27,145-28,236; 3,772,234; 4,116,917; 4,687,815; and 4,880,878. Other non-patent publications related to S-EB-S polymers include: (1) W. P. Gergen, "Uniqueness of Hydrogenated Block Copolymers for Elastomeric Applications," presented at the German Rubber

Meeting, Wiesbaden, 1983; Kautsch, Gummi, Kunstst. 37, 284 (1984). (2) W.P. Gergen, et al., "Hydrogenated Block Copolymers," Paper No. 57, presented at a meeting of the Rubber Division ACS, Los Angeles, April 25, 1985. Encyclopedia of Polymer Science and Engineering, Vol. 2, pp 324-434, "Block Copolymers". (3) L. Zotteri and et al., "Effect of hydrogenation on the elastic properties of poly(styrene-b-diene-b-styrene) copolymers", Polymer, 1978, Vol. 19, April. (4) J. Kenneth Craver, et al., Applied Polymer Science, Ch. 29, "Chemistry and Technology of Block Polymers", pp. 394-429, 1975. (5) Y. Mahajer and et al., "The influence of Molecular Geometry on the Mechanical Properties of homopolymers and Block Polymers of Hydrogenated Butadiene and Isoprene" reported under U.S. ARO Grant No. DAAG29-78-G-0201. (6) J. E. McGrath, et al., "Linear and Star Branched Butadiene-Isoprene Block Copolymers and Their Hydrogenated Derivatives", Chem. Dept, Virginia Polytechnic Institute and State University Blacksturg, VA, reported work supported by Army Research Office. (7) Legge, Norman R., "Thermoplastic Elastomers", Charles Goodyear Medal address given at the 131st Meeting of the Rubber Division, American Chemical Society, Montreal, Quebec, Canada, Vol. 60, G79-G115, May 26-29, 1987. (8) Falk, John Carl, and et al., "Synthesis and Properties of Ethylene-Butylene-1 Block Copolymers", Macromolecules, Vol. 4, No. 2, pp. 152-154, March-April 1971. (9) Morton, Maurice, and et al., "Elastomeric Polydiene ABA Triblock Copolymers within Crystalline End Blocks", University of Arkon, work supported by Grant No. DMR78-09024 from the National Science Foundation and Shell Development Co. (10) Yee, A. F., and et al., "Modification of PS by S-EB-S Block Copolymers: Effect of Block Length", General Electric Corporate Research & Development, Schenectady, NY 12301. (11) Siegfried, D. L., and et al., "Thermoplastic Interpenetrating Polymer Networks of a Triblock Copolymer elastomer and an Ionomeric Plastic Mechanical Behavior", Polymer Engineering and Science, Jan. 1981, Vol. 21, No.1, pp 39-46. (12) Clair, D. J., "S-EB-S Copolymers Exhibit Improved Wax Compatibility", Adhesives Age, November, 1988. (13) Shell Chemical Technical Bulletin SC:1102-89, "Kraton® Thermoplastic Rubbers in oil gels", April 1989. (14) Chung P. Park and George P. Clingerman, "Compatibilization of Polyethylene-Polystyrene Blends with Ethylene-Styrene Random Copolymers", the Dow Chemical Company, May 1996. (15) Steve Hoenig, Bob Turley and Bill Van Volkenburgh, "Material Properties and Applications of Ethylene-Styrene Interpolymers", the Dow Chemical Company, September 1996. (16) Y. Wilson Cheung and Martin J. Guest, "Structure, Thermal Transitions and Mechanical Properties of Ethylene/Styrene Copolymers", the Dow Chemical Company, May 1996. (17) Teresa Plumley Karjaia, Y. Wilson Cheung and Martin J. Guest, "Melt Rheology and Processability of Ethylene/Styrene Interpolymers", the Dow Chemical Company, May 1997. (18) D. C. Prevorsek, et al., "Origins of Damage Tolerance in Ultrastrong Polyethylene Fibers and Composites:, Journal of Polymer Science: Polymer Symposia No. 75, 81-104 (1993). (19) Chen, H., et al, "Classification of Ethylene-Styrene Interpolymers Based on Comonomer Content", J. Appl. Polym. Sci., 1998, 70, 109. (20-24) US Patent 5,872,201; 5,460,818; 5,244,996; EP 415815A; JP07,278,230 describes substantially random, more appropriately presudo-random copolymers (interpolymers), methods of making and their uses. (25) Alizadeh, et al., "Effect of Topological Constraints on The Crystallization Behavior of Ethylene/alp[ha-

Olefin Copolymers", PMSE, Vol, 81, pp. 248-249, August 22-26, 1999. (26) Guest, et al., "Structure/Property Relationships of Semi-Crystalline Ethylene-Styrene Interpolymers (ESI)", PMSE, Vol, 81, pp. 371-372, August 22-26, 1999. The above applications, patents and publications are specifically incorporated herein by reference.

Legge's paper teaches the development of (conventional substantially amorphous elastomer midsegment) SEBS triblock copolymers. In the polymerization of butadiene by alkylithium initiators, 1,4-addition or 1,2-addition polymers, mixtures, can be obtained. In forming styrene butadiene triblock copolymers involving the addition of solvating agents such as ethers just before the final styrene charge is added, any excess of ethers can alter the polybutadiene structure from a 1,4-cis or trans structure to a 1,2- or 3,4-addition polymer. Using difunctional coupling agent would give linear block copolymers and multifuntional agents would give star-shaped or radial block copolymers. Hydrogenation of the 1,4-polybutadiene structure yields polyethylene, while that of the 1,2-polybutadiene yields polybutylene. The resulting polyethylene will be essentially identical with linear, high-density polyethylene with a melting point, Tm, of about 136oC. Hydrogenation of 1,2-polybutadiene would yield atactic poly(1-butene) (polybutylene). The Tg of polybutylene is around -18oC. Random mixtures of ethylene and butylene units in the chain would suppress crystallinity arising from polyethylene sequences. The objective for a good elastomer should be to obtain a saturated olefin elastomeric segment with the lowest possible Tg and the best elastomeric properties. Such an elastomer favored using styrene as the hard-block monomer and selecting the best monomer for hydrogenation of the elastomer midsegment. Using a mixture of 1,4- and 1,2-polybutadiene as the base polymer for the midsegment would result in an ethylene/butylene midsegment in the final product. The elements of selection of the midsegment composition is elastomer crystallinity and the elastomer Tg of an ethylene/butylene copolymer. Very low levels of crystallinity can be achieved around 40-50% butylene concentration. The minimum in dynamic hysteresis around 35% butylene concentration in the elastomeric copolymer. A value of 40% butylene concentration in the ethylene/butylene midsegment was chosen for the S-EB-S block copolymers.

Clair's paper teaches that the EB midblock of conventional S-EB-S polymers is a random copolymer of ethylene and 1-butene exhibiting nearly no crystallinity in the midblock. In the preparation of ethylene-butylene (EB) copolymers, the relative proportions of ethylene and butylene in the EB copolymer chain can be controlled over a broad range from almost all ethylene to almost all butylene. When the EB copolymer is nearly all ethylene, the methylene sequences will crystallize exhibiting properties similar to low density polyethylene. In differential scanning calorimeter (DSC) curves, the melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. As the amount of butylene in the EB copolymer is increased, the methylene sequences are interrupted by the ethyl side chains which shorten the methylene sequences length so as to reduce the amount of crystallinity in the EB copolymer. In conventional S-EB-S polymers, the amount of 1-butene is controlled at a high enough level to make the EB copolymer midblock almost totally amorphous so as to make the copolymer rubbery and soluble in hydrocarbon solvents. Clair suggests that an S-EB-S polymer retaining at least some crystallinity in the EB

copolymer midblock may be desirable. Therefore, a new family of S-EB-S polymers are developed (U.S. Patent No. 3,772,234) in which the midblock contains a higher percentage of ethylene. The molecular weights of the new crystalline midblock segment S-EB-S polymers can vary from low molecular weight, intermediate molecular, to high molecular weight; these are designated Shell GR-3, GR-1, and GR-2 respectively. Unexpectly, the highest molecular weight polymer, GR-2 exhibits an anomalously low softening point. A broad melting endotherm is seen in the DSC curves of these polymers. The maximum in this broad endotherm occurs at about 40oC.

Himes, et al., (4,880,878) describes SEBS blends with improved resistance to oil absorption.

Papers (14) - (17) describes poly(ethylene-styrene) substantially random copolymers (Dow Interpolymers™): Dow S, M and E Series produced by metallocene catalysts, using single site, constrained geometry addition polymerization catalysts resulting in poly(ethylene-styrene) substantially random copolymers with weight average molecular weight (Mw) typically in the range of 1×10^5 to 4×10^5, and molecular weight distributions (Mw/Mn) in the range of 2 to 5.

Paper (18) Prevorsek, et al., using Raman spectroscopy, WAXS, SAXD, and EM analysis interprets damage tolerance of ultrastrong PE fibers attributed to the nano scale composite structure that consists of needle-like- nearly perfect crystals that are covalently bonded to a rubbery matrix with a structure remarkably similar to the structure of NACRE of abalone shells which explains the damage tolerance and impact resistance of PE fibers. PE because of its unique small repeating unit, chain flexibility, ability to undergo solid state transformation of the crystalline phase without breaking primary bonds, and its low glass transition temperature which are responsible for large strain rate effects plays a key role in the damage tolerance and fatigue resistance of structures made of PE fibers.

Chen (19) classifies 3 distinct categories of E (approximately 20-50 wt% styrene), M (approximately 50-70 wt% styrene), & S (greater than approximately 70 wt% styrene) substantially random or more appropriately pseudo-random ethylene-styrene copolymers or random copolymers of ethylene and ethylene-styrene dyads. The designated Ethylene-styrene copolymers are: E copolymers (ES16, ES24, ES27, ES28, ES30, and ES44 with styrene wt% of 15.7, 23.7, 27.3, 28.1, 39.6 & 43.9 respectively), M copolymers (ES53, ES58, ES62, ES63, and ES69 with styrene wt% of 52.5, 58.1, 62.7, 62.8, and 69.2 respectively and crystallinity, %, DSC, based on copolymer of 37.5, 26.6, 17.4, 22.9, 19.6 and 5.0 respectively) , S copolymers (ES72, ES73, and ES74 with styrene wt% of 72.7, 72.8, and 74.3 respectively). The maximum comonomer content for crystallization of about 20% is similar in other ethylene copolymers, such as in ethylene-hexene and ethylene-vinyl acetate copolymers. If the comonomer can enter the crystal lattice, such as in ethylene-propylene, compositions in excess of 20 mol % comonomer can exhibit crystallinity. The molecular weight distribution of these copolymers is narrow, and the comonomer distribution is homogeneous. These copolymers exhibit high crystalline, lamellar morphologies to fringed micellar morphologies of low crystallinity. Crystallinity is determined by DSC measurements using a Rheometric DSC. Specimens weighing between 5 and 10 mg are heated from -80 to 180oC at a rate of 10oC/min (first heating), held at 190oC for 3 min, cooled to -80oC at 10oC/min, held at

-80oC for 3 min, and reheated from -80oC to 180oC at 10oC/min (second heating). The crystallinity (wt%) is calculated from the second heating using a heat of fusion of 290 J/g for the polyethylene crystal. Contributing effects of the crystallinity include decrease volume fraction of the amorphous phase, restricted mobility of the amorphous chain segments by the crystalline domains, and higher styrene content of the amorphous phase due to segregation of styrene into the amorphous phase. Table I of this paper shows values of Total Styrene (wt%), aPS (wt%), Styrene (wt%), Styrene (mol %), 10^{-3}Mw, Mw/Mn, and Talc (wt%) for Ethylene-styrene copolymers ES16-ES74 while Figs 1-12 of this paper shows: (1) melting thermograms of ESI 1st and 2nd heating for ES16, ES27, ES44, ES53, ES63, & ES74; (2) crystallinity from DSC as a function of conmonomer content; (3) Logarithmic plot of the DSC heat of melting vs. Mole % ethylene for ESIs; (4) measured density as a function of styrene content for semicrystalline and amorphous ESIs; (5) % crystallinity from density vs % crystallinity from DSC melting enthalpy; (6) Dynamic mechanical relaxation behavior; (7) Glass transition temperature as a function of wt % ethylene-styrene dyads for semicrystalline and amorphous ESIs; (8) Arrhenius plots of the loss tangent peak temperature for representative semicrystalline and amorphous ESIs; (9) Draw ratio vs engineering strain; (10) Engineering stress-strain curves at 3 strain rates for ES27, ES63 and ES74; (11) Engineering stress-strain curves of ESIs; (12) Classification scheme of ESIs based on composition.

(20) US Patent 5,872,201 describes interpolymers: terpolymers of ethylene/styrene/propylene, ethylene/styrene/4-methyl-1-pentene, ethylene/styrene/hexend-1, ethylene/styrene/octene-1, and ethylene/styrene/norbornene with number average molecular weight (Mn) of from 1,000 to 500,000.

(21-24) US Patents 5,460,818; 5,244,996; EP 415815A; JP07,278,230 describes substantially random, more appropriately presudo-random copolymers (interpolymers), methods of making and their uses.

(25) Alizadeh, et al., find the styrene interpolymers impedes the crystallization of shorter ethylene crystallizable sequences and that two distinct morphological features (lamellae and fringe micellar or clain clusters) are observed in ethylene/styrene (3.4 mol%) as lamella crystals organized in stacks coexisting with interlamellar bridge-like structures.

(26) Guest, et al., describes ethylene-styrene copolymers having less than about 45 wt % copolymer styrene being semicrystalline, as evidenced by a melting endotherm in DSC testing (Dupont DSC-901, 10oC/min) data from the second heating curve. Crystallization decreases with increasing styrene content. Based on steric hindrance, styrene unit is excluded from the crystalline region of the copolymers. Transition from semi-crystalline to amorphous solid-state occurs at about 45 to 50 wt % styrene. At low styrene contents (<40%), the copolymers exhibit a relatively well-defined melting process. Figs 1-5 of this paper shows (a) DSC data in the T range associated with the melting transition for a range of ESI differing primarily in copolymer styrene content, (b) variation in percent crystallinity (DSC) for ESI as a function of copolymer S content, (c) elastic modulus versus T for selected ESI differing in S content, (d) loss modulus versus T for selected ESI differing in S content, (e) Tensile stress/strain behavior of ESI differing in S content, respectively. The above patents and publications are specifically incorporated herein

by reference.

Prior amorphous gels made from SEPS and SEBS are inadequate for the most demanding applications involving endurance at high stress and strain levels over an extended period of time exhibiting greater strain under elongation which are essential for the gels to have uses as artificial muscles.

The crystal gels which are advantageously useful for making artifical muscles, toys, medical devices, and other useful articles of manufacture including disposable inflatable restraint cushions, and especially for use as artificial muscles, and the like. Said crystal gels comprises: 100 parts by weight of one or more high viscosity (I) linear triblock copolymers, (II) multi-arm block copolymers, (III) branched block copolymers, (IV) radial block copolymers, (V) multiblock copolymers, (VI) random copolymers, (VII) thermoplastic crystalline polyurethane copolymers with hydrocarbon midblocks or mixtures of two or more (I)-(VII) copolymers in combination with or without major or minor amounts of one or more other (VIII) copolymers or polymers, said copolymers having one or more segments or one or more midblocks comprising one or more substantially crystalline polyethylene segments or midblocks and selected amounts of a compatible plasticizer (IX) sufficient to achieve gel rigidities of from less than about 2 gram Bloom to about 1,800 gram Bloom and higher with the proviso that when said (I)-(VII) copolymers having nil amorphous segment or nil amorphous midblock are combined with one or more (VIII) copolymers having one or more amorphous segments or amorphous midblocks to form a stable plasticizer compatible gel.

With respect to the random copolymers (VI) embodiments forming the crystal gels of the invention, such crystal gels comprises:

(i) one or more substantially random copolymers (pseudo-random copolymers or interpolymers) having one or more glassy components and at least one substantially crystalline components, wherein said (i) copolymers being in combination with a selected amount of one or more selected second copolymers comprising:

(ii) one or more substantially random copolymers having one or more glassy components and one or more crystalline components of moderate crystallinity;

(iii) one or more substantially random copolymers having one or more glassy components and one or more crystalline components of low crystallinity;

(iv) one or more substantially random copolymers having one or more glassy components and one or more amorphous components;

(v) one or more of a diblock, triblock, multi-arm block, branched block, radial block, or multiblock copolymers, wherein said (v) copolymers having one or more glassy components and one or more elastomeric components of selected crystallinity; and

(vi) one or more of a diblock, triblock, multi-arm block, branched block, radial block, or multiblock copolymers, wherein said (vi) copolymers having one or more glassy components and one or more amorphous elastomeric components;

(vii) a mixture of two or more (ii)-(vi) copolymers;

wherein said (i)-(iii) and (v) copolymers are characterized by sufficient crystallinity as to exhibit a melting

endotherm of at least about 25°C as determined by DSC curve, and said crystal gel being characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 10°C as determined by DSC curve;

(II) in combination with or without one or more of selected homopolymers; and

(III) a selected amount of one or more compatible plasticizers of sufficient amounts to achieve a stable gel having rigidities of from less than about 2 gram Bloom to about 1,800 gram Bloom.

The gels comprising the thermoplastic elastomer copolymers and block copolymers having one or more substantially crystalline polyethylene segments or midblocks of the invention are hereafter referred to as "elastic-crystalline gels" or simpler "crystal gels". The crystalline copolymers are characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 25°C as determined by DSC curve, and said crystal gel being characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 10°C as determined by DSC curve.

The various types of copolymers and block copolymers employed in forming the crystal-gels of the invention are of the general configurations (Y-AY)n copolymers, A-Z-A, and (A-Z)n block copolymers, wherein the subscript n is a number of two or greater. In the case of multiarm block copolymers where n is 2, the block copolymer denoted by (A-Z)n is A-Z-A. It is understood that the coupling agent is ignored for sake of simplicity in the description of the (A-Z)n block copolymers.

The segment (A) comprises a glassy amorphous polymer end block segment which can be polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstryene), poly(p-methylstyrene) and the like, preferably, polystyrene.

The segment (Y) of copolymers (Y-AY)n comprises substantially crystalline poly(ethylene) (simply denoted by "-E-" or (E)). In the case of copolymers (A-Y)n, (Y) when next to (A) may be substantially non-crystalline or amorphous ethylene segments. For example a crystalline copolymer (Y-AY)n may be represented by:.... -E-E-E-E-E-E-E-E-E-SE-E-E-E-E-E-E-SE-E-E-E-E-E-E-SE-.... Where Y is a long run of polyethylene or a non-crystalline copolymer (AY-AY)n: ...-E-SE-SE-E-SE-E-SE-E-SE-E-E-SE-SE-E-SE-...., where Y is a non-crystalline run of ethylene.

Other substantially random copolymers suitable for forming crystal gels of the invention include (Y-A-Y') where Y is a crystalline run of ethylene and Y' can be propylene, 4-methyl-1-pentene, hexene-1, octene-1, and norborene. A can be styrene, vinyl toluene, alpha-methylstyrene, t-butylstyrene, chlorostyrene, including isomers and the like. Examples are: poly(ethylene-styrene) (ES), poly(ethylene-styrene-propylene) (ESP), poly(ethylene-styrene-4-methyl-1-pentene) (ES4M1P), poly(ethylene-styrene-hexend-1) (ESH1), poly(ethylene-styrene-octene-1) (ESO1), and poly(ethylene-styrene-norborene) (ESN), poly(ethylene-alpha-methylstyrene-propylene), poly(ethylene-alpha-methylstyrene-4-methyl-1-pentene), poly(ethylene-alpha-methylstyrene-hexend-1), poly(ethylene-alpha-methylstyrene-octene-1), and poly(ethylene-alpha-methylstyrene-norborene) and the like.

The end block segment (A) comprises a glassy amorphous polymer end block segment which can be polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstryene), poly(p-

methylstyrene) and the like, preferably, polystyrene. The segment (Y) of random copolymers A-Y comprises substantially crystalline poly(ethylene) (simply denoted by "-E-" or (E)). In the case of random copolymers A-Y, (Y) may be substantially non-crystalline or amorphous ethylene segments. The midblocks (Z) comprises one or more midblocks of substantially crystalline poly(ethylene) (simply denoted by "-E- or (E)") with or without one or more amorphous midblocks of poly(butylene), poly(ethylene-butylene), poly(ethylene-propylene) or combination thereof (the amorphous midblocks are denoted by "-B- or (B)", "-EB- or (EB)", and "-EP- or (EP)" respectively or simply denoted by "-W- or (W)" when referring to one or more of the amorphous midblocks as a group) The A and Z, and A and Y portions are incompatible and form a two or more-phase system consisting of sub-micron amorphous glassy domains (A) interconnected by (Z) or (Y) chains. The glassy domains serve to crosslink and reinforce the structure. The number average molecular weight (Mn) of the random copolymers is preferably greater than 1,000, advantageously from about 5,000 to about 1,100,000, more advantageously from abut 8,000 to about 700,000. Examples are:

The method of making Y-A-Y and Y-A-Y' random copolymers by metallocene single site catalysts are described in US Patent No. 5871201, 5470993, 5055438, 5057475, 5096867, 5064802, 5132380. 5189192, 5321106, 5347024, 5350723, 5374696, 5399635, and 5556928, 5244996, application EP-A-0416815, EP-A-514828, EP-A-520732, WO 94/00500 all of which disclosure are incorporated herein by reference.

The linear block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30oC of from less than about 40 cps to about 60 cps and higher, advantageously from about 40 cps to about 160 cps and higher, more advantageously from about 50 cps to about 180 cps and higher, still more advantageously from about 70 cps to about 210 cps and higher, and even more advantageously from about 90 cps to about 380 cps and higher.

The branched, star-shaped (radial), or multiarm block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30oC of from about 80 cps to about 380 cps and higher, advantageously from about 150 cps to about 260 cps and higher, more advantageously from about 200 cps to about 580 cps and higher, and still more advantageously from about 100 cps to about 800 cps and higher.

The poly(ethylene/styrene) copolymers, type S series has more than 50 wt% styrene and is glassy at short times and rubbery at long times and exhibits ambient Tg, melt density of about higher than 0.952 to about 0.929 and less, typical Mw = about less than 150,000 to 350,000 and higher.

The type M series has more than 50 wt% styrene is amorphous rubber and exhibits very low modulus, high elasticity, low Tg of from greater than 10oC to less than -50oC, melt Index of from higher than 5 to less than about 0.1, melt density of higher than 0.93 to 9.0 and less, typical Mw = about less than 200,000 to 300,000 and higher.

The type E series contains up to 50 wt% styrene is semi-crystalline rubber and exhibits low Tg of from greater than 0oC to about less than -70, low modulus semi-crystalline, good compression set, Melt

Index of from about higher than 2 to less than 0.03, melt density of about higher than 0.90 to 0.805 and less, Mw = about less than 250,000 to 350,000 and higher.

The E series random copolymers can be blended with the type M and type S series copolymers (having high glassy components) and one or more of the i, ii, iii, iv, v, vii and viii copolymers, plasticizers to form crystalline polymer Crystal gels of the invention.

This physical elastomeric network structure is reversible, and heating the polymer above the softening point of the glassy domains temporarily disrupt the structure, which can be restored by lowering the temperature. During mixing and heating in the presence of compatible plasticizers, the glassy domains (A) unlock due to both heating and solvation and the molecules are free to move when shear is applied. The disruption and ordering of the glassy domains can be viewed as a unlocking and locking of the elastomeric network structure. At equilibrium, the domain structure or morphology as a function of the (A) and (Z) or (A) and (Y) phases (mesophases) can take the form of spheres, cylinders, lamellae, or bicontinous structures. The scale of separation of the phases are typically of the order of hundreds of angstroms, depending upon molecular weights (i.e. Radii of gyration) of the minority-component segments. At such small domain scales, when the gel is in the molten state while heated and brought into contact to be formed with any substrate and allowed to cool, the glassy domains of the gel become interlocked with the surface of the substrate. At sufficiently high enough temperatures, with or without the aid of other glassy resins, the glassy domains of the copolymers forming the gels fusses and interlocks with even a visibly smooth substrate surface such as glass. The disruption of the sub-micron domains due to heating above the softening point forces the glassy domains to open up, unlocking the network structure and flow. Upon cooling below the softing point, the glassy polymers reforms together into sub-micron domains, locking into a network structure once again, resisting flow. It is this unlocking and locking of the network structure on the sub-micron scale with the surfaces of various materials which allows the gel to form interlocking composites with other materials. Such interlocking with many different materials produce gel composites having many uses.

The (I) linear block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30oC of from less than about 40 cps to about 60 cps and higher, advantageously from about 40 cps to about 160 cps and higher, more advantageously from about 50 cps to about 180 cps and higher, still more advantageously from about 70 cps to about 210 cps and higher, and even more advantageously from about 90 cps to about 380 cps and higher.

The (II, IV, and V) branched, star-shaped (radial), or multiarm block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30oC of from about 80 cps to about 380 cps and higher, advantageously from about 150 cps to about 260 cps and higher, more advantageously from about 200 cps to about 580 cps and higher, and still more advantageously from about 100 cps to about 800 cps and higher.

The crystal gels can be made in combination with a selected amount of one or more selected polymers and copolymers (II) including thermoplastic crystalline polyurethane elastomers with

hydrocarbon blocks, homopolymers, copolymers, block copolymers, polyethylene copolymers, polypropylene copolymers, and the like described below.

The crystal gels of the invention are also suitable in physically interlocking or forming with other selected materials to form composites combinations. The materials are selected from the group consisting of paper, foam, plastic, fabric, metal, metal foil, concrete, wood, glass, various natural and synthetic fibers, including glass fibers, ceramics, synthetic resin, and refractory materials.

The high tear resistant soft crystal gels are advantageously suitable for a safer impact deployable air bag cushions, the higher tear resistant crystal gels are advantageously more suitable, and the highest tear resistant crystal gels are advantageously even more suitable for such use and other uses. As impact deployable air bag cushions under expansion exhibit greater strain, the greater strain property makes also a better artificial muscle.

Very thin films of the crystal gels of the invention are suitable for use as artificial muscles in the form of thin films wrapped into a cylinder. The crystal gel film stretch when one side of a film is given a positive charge and the other a negative. The charges cause each wrapped film to contract toward the center of the cylinder which forces the cylinder to expand lengthwise. When the power supply is off, the cylindrical muscles relaxes. Thus, the roll up gel can push, pull, and lift loads.

A thin films or membrane of the crystal gels having a thickness of about 5 mm to less than 0.1 mm are useful as artificial muscles. Film thickness of from .005 mm, .01 mm, .02 mm, .03 mm, .04 mm, .05 mm, .06 mm, .07 mm, .08 mm, .09 mm, .10 mm, .2 mm, .3 mm, .4 mm, .5 mm, .6 mm, .7 mm, .8 mm, .9 mm, 1.0 mm, 1.1 mm, 1.2 mm, 1.3 mm, 1.4 mm, 1.5 mm, 1.6 mm, 1.7 mm, 1.8 mm, 1.9 mm, 2.0 mm, 2.1 mm, 2.2 mm, 2.3 mm, 2.4 mm, 2.5 mm, 2.6 mm, 2.7 mm, 2.8 mm, 2.9 mm, 3.0 mm, 3.1 mm, 3.2 mm, 3.3 mm, 3.4 mm, 3.5 mm, 3.6 mm, 3.7 mm, 3.8 mm, 3.9 mm , 4.0 mm can be utilized for forming artificial muscles of the invention.

Fine powder of the common transition metals can be utilized as a coating electrodes on the top and bottom flat sides of the crystal gel film to serve as conductor, such as aluminum, alpha aluminum, copper, silver, gold, tin, nickel, iron, cobalt, zinc, lead, and the like.

We denote "|" as a crystal gel film layer, G, and "||" as two crystal gel film layers, GG, side by side, "|||" as three crystal gel film layers, GGG, side by side. We denote E as a metal electrode or conductor electrode on both sides of the G film layer, such as EGE, EGEGE, EGEGEGE, EGEGEGEGE and the like. We denote (+) as a positive charge, (-) as a negative charge. We then denote the single charged membrane or film layer as "(+)E|E(-)" showing a single crystal gel layer with electrodes on both sides and a positive charge on its left side and a negative charge on its right side. Hence "(+)E|E(-)(-)E|E(+)", denotes a double crystal gel thin film layers with electrodes on each side of the film layers and charged from left to right as positive, negative, negative, and positive. This arrangement allows for the rolling up of the double layers into a cylindrical cylinder without discharging the double layers by rolling unto itself. Another way of rolling up a thin crystal gel film "(+)E|E(-)" require folding the (-) side with the (-) sides as a continuous S curve layers upon layers and then rolling the S curve so that the same

charged sides roll unto itself into a cylinder. Other combination can be made for use as charged thin film layers for artificial muscle use, such as

a) (+)E|E(-),

b) (+)E|E(-)(-)E|E(+),

c) (+)E|E(-)(-)E|E(+)(+)E|E(-),

d) (+)E|E(-)(-)E|E(+)(+)E|E(-)(-)E|E(+), and

e) (+)E|E(-)(-)E|E(+)(+)E|E(-)(-)E|E(+)(+)E|E(-).

Moreover, the crystal gels films can be formed as composite multiple layers of films with separating electrical conducting layer with encapsulated connectors for easy folding.

The diameter of the rolled up gel cylinder can be from about 1 mm to abut 8 mm, suitably, about 0.5 mm to about 5 mm, more suitably about 1 mm to about 3 mm. Generally the rolled up diameter can be from less than 0.5 mm to about 12 mm or larger. The length of the cylinder can be almost any suitable length, from about 5 mm to about 50 mm, suitably, 8 mm to 20 mm, more suitably from less than 8 mm to 12 mm and longer.

Conductive connectors (of foil, polymer, or conductive gel) can be attached to the inner and outer electrodes respectively. The Direct current voltage from a power supply can be applied which voltage can range from less than 100 volts to greater than 10,000 volts. Voltages of 1,000v, 2,000v, 3,000v, 4,000v, 5,000v, 6,000v, 7,000v, 8,000v, 9,000v, 10,000v, 12,000v, 15,000v, 18,000v can also be used. The voltages can be regulated selectively by hand or an electronic timer from less than one thousands of a second to minutes, hours, and days duration. Electrical timing of the applied voltages can range from a few micro seconds and longer.

The crystal gel film can be made by conventional extrusion, hot melt spin coating, casting, dipping and the like. The artificial muscle made in this manner are useful as contractible muscle elements for small robots which crystal gel film, contracts in thickness and extends in length and width due to the electrostatic forces when a voltage is applied. The crystal gel cylinder increases and decreases in volume thickness so as to expand and contract lengthwise due to the electrostatic forces of the charges on the opposite dielectric surfaces of the gel film. This effect is a function of the dielectric constant of the crystal gel. In order to provide for a muscle with a large strain and therefore a large actuation pressure (greater than 5 MPa). The performance, efficiency and faster response of the cylindrical muscle depends on the amount of strain obtained under elongation. The higher strain under elongation, the better the performance, the better the efficiency, and the faster the response.

Crystal gel muscles actuators made from thin films having greater polyethylene crystallinity are found to produces greater performance, greater efficiency, and faster response than amorphous gels. This result is due to the greater strain performance under elongation. The elongation of the crystal gels of the invention can range from

about 100% to greater than 3,000 %. The actuation pressure of the actuators made from the crystal gels of the invention can range from about 5 MPa to greater than about 12 MPa. As an example, a 15 layer

rolled/folded crystal gel film actuator having a active muscle length of 10 mm and a diameter of 3 mm (made from 0.5 mm thick SEEPS 500 gram Bloom gel) can achieve a stroke of at least about 3 mm and a force of at least about 5 grams.

The strain under elongation of the copolymers forming the crystal gels can range from less than 8 MPa to about 18 MPa and higher as measure at a strain rate of 1000%/min., from less than 5 MPa to about 25 MPa and higher as measure at a strain rate of 100%/min., and from less than 5 MPa to about 30 MPa and higher as measure at a strain rate of 10%.min. Reference (19) reports the fracture strain% and corresponding modulus (Mpa) for Ethylene-styrene copolymers ES16, ES24, ES27, ES28, ES28, and ES30 are 666/52.5, 517/26.4, 453/25, 564/19.5 and 468/25.4 respectively.

The ability to reduce the number of layers, increase strain with elongation, reduce the size of the active muscle actuator and increase the stroke distance at a greater force can be achieved with crystal gels (exhibiting high strain under elongation) made from copolymers having one or more crystalline components.

The crystal gels of the invention can be formed into gel strands, gel tapes, gel sheets, films, and other articles of manufacture in combination with or without other substrates or materials such as natural or synthetic fibers, multifibers, fabrics, films and the like. Moreover, because of their improved tear resistance and resistance to fatigue, the crystal gels exhibit versatility as balloons for medical uses, such as balloon for valvuloplasty of the mitral valve, gastrointestinal balloon dilator, esophageal balloon dilator, dilating balloon catheter use in coronary angiogram and the like. Since the crystal gels are more tear resistant, they are especially useful for making condoms, toy balloons, and surgical and examination gloves. As toy balloons, the crystal gels are safer because it will not rupture or explode when punctured as would latex balloons which often times cause injures or death to children by choking from pieces of latex rubber. The crystal gels are advantageously useful for making gloves, thin gloves for surgery and examination and thicker gloves for vibration damping which prevents damage to blood capillaries in the fingers and hand caused by handling strong shock and vibrating equipment. The crystal gels are also useful for forming orthotics and prosthetic articles such as for lower extremity prosthesis described below.

The EB copolymer midblock of conventional SEBS is almost totally amorphous and the EP midblock of SEPS is amorphous and non-crystalline.

Gels made from such block copolymers are rubbery and exhibit substantially no hysteresis. Their rubbery-ness and lack of hysteresis are due to the amorphous nature of their midblocks. Such gels are hereafter referred to as "non-crystalline gels" or more simply as "amorphous gels".

In general, the overall physical properties of amorphous gels are better at higher gel rigidities. The amorphous gels, however, can fail catastrophically when cut or notched while under applied forces of high dynamic and static deformations, such as extreme compression, torsion, high tension, high elongation, and the like. Additionally, the development of cracks or crazes resulting from a large number of deformation cycles can induce catastrophic fatigue failure of amorphous gel composites, such as tears and rips between the surfaces of the amorphous gel and substrates or at the interfaces of interlocking

material(s) and gel. Consequently, such amorphous gels are inadequate for the most demanding applications involving endurance at high stress and strain levels over an extended period of time.

This physical elastomeric network structure is reversible, and heating the polymer above the softening point of the glassy domains temporarily disrupt the structure, which can be restored by lowering the temperature. During mixing and heating in the presence of compatible plasticizers, the glassy domains (A) unlock due to both heating and solvation and the molecules are free to move when shear is applied. The disruption and ordering of the glassy domains can be viewed as a unlocking and locking of the elastomeric network structure. At equilibrium, the domain structure or morphology as a function of the (A) and (Z) or (A) and (Y) phases (mesophases) can take the form of spheres, cylinders, lamellae, or bicontinous structures. The scale of separation of the phases are typically of the order of hundreds of angstroms, depending upon molecular weights (i.e. Radii of gyration) of the minority-component segments. The sub-micron glassy domains which provides the physical interlocking are too small to see with the human eye, too small to see using the highest power optical microscope and only adequately enough to see using the electron microscope. At such small domain scales, when the gel is in the molten state while heated and brought into contact to be formed with any substrate and allowed to cool, the glassy domains of the gel become interlocked with the surface of the substrate. At sufficiently high enough temperatures, with or without the aid of other glassy resins (such as polystyrene homopolymers and the like), the glassy domains of the copolymers forming the gels fusses and interlocks with even a visibly smooth substrate surface such as glass. The disruption of the sub-micron domains due to heating above the softening point forces the glassy domains to open up, unlocking the network structure and flow. Upon cooling below the softing point, the glassy polymers reforms together into sub-micron domains, locking into a network structure once again, resisting flow. It is this unlocking and locking of the network structure on the sub-micron scale with the surfaces of various materials which allows the gel to form interlocking composites with other materials.

A useful analogy is to consider the melting and freezing of a water saturated substrate, for example, foam, cloth, fabric, paper, fibers, plastic, concrete, and the like. When the water is frozen, the ice is to a great extent interlocked with the substrate and upon heating the water is able to flow. Furthermore, the interlocking of the ice with the various substrates on close examination involves interconnecting ice in, around, and about the substrates thereby interlocking the ice with the substrates. A further analogy, but still useful is a plant or weed well established in soil, the fine roots of the plant spreads out and interconnects and forms a physical interlocking of the soil with the plant roots which in many instances is not possible to pull out the plant or weed from the ground without removing the surrounding soil also.

Likewise, because the glassy domains are typically about 200 Angstroms in diameter, the physical interlocking involve domains small enough to fit into and lock with the smallest surface irregularities, as well as, flow into and flow through the smallest size openings of a porous substrate. Once the gel comes into contacts with the surface irregularities or penetrates the substrate and solidifies, it becomes difficult or

impossible to separate it from the substrate because of the physical interlocking. When pulling the gel off a substrate, most often the physically interlocked gel remains on the substrate. Even a surface which may appear perfectly smooth to the eye, it is often not the case. Examination by microscopy, especially electron microscopy, will show serious irregularities. Such irregularities can be the source of physical interlocking with the gel.

Such interlocking with many different materials produce gel composites having many uses. The high tear resistant soft crystal gels are advantageously suitable for a safer impact deployable air bag cushions, other uses include: toys; games; novelty, or souvenir items; elastomeric lenses, light conducing articles, optical fiber connectors; athletic and sports equipment and articles; medical equipment and articles including derma use and for the examination of or use in normal or natural body orifices, health care articles; artist materials and models, special effects; articles designed for individual personal care, including occupational therapy, psychiatric, orthopedic, podiatric, prosthetic, orthodontic and dental care; apparel or other items for wear by and on individuals including insulating gels of the cold weather wear such as boots, face mask, gloves, full body wear, and the like have as an essential, direct contact with the skin of the body capable of substantially preventing, controlling or selectively facilitating the production of moisture from selected parts of the skin of the body such as the forehead, neck, foot, underarm, etc; cushions, bedding, pillows, paddings and bandages for comfort or to prevent personal injury to persons or animals; housewares and luggage; articles useful in telecommunication, utility, industrial and food processing, and the like as further described herein.

Health care devices such as face masks for treatment of sleep disorder require non-tacky crystal gels of the invention. The crystal gel 3 forming a gel overlap 7 portion on the face cup 1 at its edge 12 conforming to the face and serve to provide comfort and maintain partial air or oxygen pressure when worn on the face during sleep. Tacky gels because of its tactile feel are undesirable for such applications.

The crystal gels of the invention can be formed into gel strands, gel bands, gel tapes, gel sheets, and other articles of manufacture in combination with or without other substrates or materials such as natural or synthetic fibers, multifibers, fabrics, films and the like. Moreover, because of their improved tear resistance and resistance to fatigue, the crystal gels exhibit versatility as balloons for medical uses, such as balloon for valvuloplasty of the mitral valve, gastrointestinal balloon dilator, esophageal balloon dilator, dilating balloon catheter use in coronary angiogram and the like. Since the crystal gels are more tear resistant, they are especially useful for making condoms, toy balloons, and surgical and examination gloves. As toy balloons, the crystal gels are safer because it will not rupture or explode when punctured as would latex balloons which often times cause injures or death to children by choking from pieces of latex rubber. The crystal gels are advantageously useful for making gloves, thin gloves for surgery and examination and thicker gloves for vibration damping which prevents damage to blood capillaries in the fingers and hand caused by handling strong shock and vibrating equipment. Various other gel articles can be made from the advantageously tear resistant gels and gel composites of the inventions include gel suction sockets, suspension belts.

The crystal gels are also useful for forming orthotics and prosthetic articles such as for lower extremity prosthesis described below.

Advantageously, the crystal gels of the invention can be made non-tacky requiring no additive. Its non-tackiness are an inherent property of the crystallinity, glassy A components, and selected low viscosity plasticizers forming the crystal gels of the invention. Such crystal gels, however, must met the following criteria:

(a) the crystal gels are made from A-Z-A, (A-Z)n, (A-Y)n, (Y-AY)n and (Y-AY')n copolymers: crystalline block copolymers and crystalline poly(ethylene-styrene) substantially random copolymers of the type S, M, and E series (for example SEEPS, S-E-EB-S, S-EB_{45}-EP-S, S-E-EB_{25}-S, S-E-EP-E-S, S-EP-E-S, S-EP-E-EP-S, E-S-E, (E-S)n, (E-S-E)n, (ESP), (ES4M1P), (ESH1), (ESO1), (ESN) and(S-E-EP)n, crystalline S-EB-S with elastomeric crystalline block:glassy block ratios of 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, and 70:30) and the like;

(b) the crystal gels are made from copolymers having crystalline poly(ethylene) segments exhibit melting endotherm values of at least about 25oC, 26oC, 27oC, 28oC, 29oC, 30oC, 31oC, 32oC, 33oC, 34oC, 35oC, 36oC, 37oC, 38oC, 39oC, 40oC, 41oC, 42oC, 43oC, 44oC, 45oC, 46oC, 47oC, 48oC, 49oC, 50oC, 51oC, 52oC, 53oC, 54oC, 55oC, 56oC, 57oC, 58oC, 59oC, 60oC, 61oC, 62oC, 63oC, 64oC, 65oC, 66oC, 67oC, 68oC, 69oC, 70oC, 71oC, 72oC, 73oC, 74oC, 75oC, 76oC, 77oC, 78oC, 79oC, 80oC, and higher; and

(c) the crystal gels are made from copolymers having glassy A to Y or glassy A to Z ratios of at least 37:63, higher ratios are also of advantage such as 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49, 52:48, 53:47, 54:46, 55:45, 56:44, 57:43, 58:42, 59:41, 60:40, 61:39, 62:38, 63:37, 64:36, 65:35, 66:34, while lower ratios may also be of advantage (but less so) such as 35:65 and 36:64; or by the addition of

(d) sufficient amounts of glassy homopolymers or glass associated phase resins so that condition (c) is met.

It is believed that the combination of sufficient amounts of crystallinity and sufficient amounts glassy A components of the copolymers in combination with low viscosity plasticizers imparts non-tackiness to the crystal gels of the invention. It is therefore contemplated that the same effect can be achieved by blending highly crystalline and highly glassy copolymers (Dow S, M, & E Series E-S-E), with less crystalline and less glassy copolymers such as amorphous SEPS, SEBS, and amorphous S-EB-EP-S and other amorphous copolymers provided the amorphous copolymers are in minor amounts and there is substantial crystallinity and sufficient over all glassy A components to meet conditions (c).

The glassy homopolymers of (d) are advantageously selected from one or more homopolymers of: polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstryene), poly(p-methylstyrene), and poly(dimethylphenylene oxide). The average molecular weight of the glassy homopolymers advantageously can range from about 2,500 to about 90,000, typical about 3,000; 4,000;

5,000; 6,000; 7,000; 8,000; 9,000; 10,000; 11,000; 12,000, 13,000; 14,000; 15,000; 16,000; 17,000; 18,000; 19,000; 20,000; 30,000; 40,000; 50,000; 60,000; 70,000; 80,000; 90,000 and the like. Example of various molecular weights of commercially available polystyrene: Aldrich Nos.: 32,771-9 (2,500M_w), 32,772-7 (4,000 Mw), 37,951-4 (13,000 Mw), 32-774-3 (20,000 Mw), 32,775-1 (35,000 Mw), 33,034-5 (50,000 Mw), 32,777-8 (90,000 Mw); poly(alpha-methylstyrene) #41,794-7 (1,300 Mw), 19,184-1 (4,000 Mw); poly(4-methylstyrene) #18,227-3 (72,000 Mw), Endex 155, 160, Kristalex 120, 140 from Hercules Chemical, GE: Blendex HPP820, HPP822, HPP823, and the like. Various glassy phase associating resins having softening points above about 120oC can also serve to increase the glassy phase of the Crystal gels of the invention and met the non-tackiness criteria, these include: Hydrogenated aromatic resins (Regalrez 1126, 1128, 1139, 3102, 5095, and 6108), hydrogenated mixed aromatic resins (Regalite R125), and other aromatic resin (Picco 5130, 5140, 9140, Cumar LX509, Cumar 130, Lx-1035) and the like.

On the other hand, the molten gelatinous elastomer composition will adhere sufficiently to certain plastics (e.g. acrylic, ethylene copolymers, nylon, polybutylene, polycarbonate, polystyrene, polyester, polyethylene, polypropylene, styrene copolymers, and the like) provided the temperature of the molten gelatinous elastomer composition is sufficient high to fuse or nearly fuse with the plastic. In order to obtain sufficient adhesion to glass, ceramics, or certain metals, sufficient temperature is also required (e.g. above 250oF). Commercial resins which can aid in adhesion to materials (plastics, glass, and metals) may be added in minor amounts to the gelatinous elastomer composition, these resins include: Super Sta-tac, Nevtac, Piccotac, Escorez, Wingtack, Hercotac, Betaprene, Zonarez, Nirez, Piccolyte, Sylvatac, Foral, Pentalyn, Arkon P, Regalrez, Cumar LX, Picco 6000, Nevchem, Piccotex, Kristalex, Piccolastic, LX-1035, and the like.

The commercial resins which can aid in adhesion to materials (plastics, glass, and metals) may be added in minor amounts to the gelatinous elastomer composition, these resins include: polymerized mixed olefins (Super Sta-tac, Betaprene Nevtac, Escorez, Hercotac, Wingtack, Piccotac), polyterpene (Zonarez, Nirez, Piccolyte, Sylvatac), glycerol ester of rosin (Foral), pentaerythritol ester of rosin (Pentalyn), saturated alicyclic hydrocarbon (Arkon P), coumarone indene (Cumar LX), hydrocarbon (Picco 6000, Regalrez), mixed olefin (Wingtack), alkylated aromatic hydrocarbon (Nevchem), Polyalphamethylstyrene/vinyl toluene copolymer (Piccotex), polystyrene (Kristalex, Piccolastic), special resin (LX-1035), and the like. More earlier, I had also disclosed the use of liquid tackifiers in high viscosity SEBS gels.

The incorporation of such adhesion resins is to provide strong and dimensional stable adherent crystal gels, gel composites, and gel articles. Typically such adherent crystal gels can be characterized as adhesive gels, soft adhesives or adhesive sealants. Strong and tear resistant adherent crystal gels may be formed with various combinations of substrates or adhere (attach, cling, fasten, hold, stick) to substrates to form adherent crystal gel/substrate articles and composites.

Various substrate and adherent crystal gel combinations (Fig. 1 - 4x.) which can be utilized to form

composite adherent crystal gel articles include: GnMn, GnGn, GnMnGn, MnGnMn, MnGnGn, GnGnMn, GnGnMn, GnMnMnGn, MnGnGnMn, MnMnGnGn, MnMnMnGnGn, GnMnGnGn, GnMnGnMnMn, MnGnMnGnMnGnMn, or any permutations of said combination, where G = gel and M = material. The subscript 1, 2, 3, 4, etc., are different and is represented by n which is a positive number, when n is a subscript of M, n may be the same or different material and when n is a subscript of G, n can be the same or different rigidity adherent crystal gel or the same or different adherent crystal gel material composition. The material (M) suitable for forming composite articles with the gelatinous elastomer compositions can include foam, plastic, fabric, metal, concrete, wood, wire screen, refractory material, glass, synthetic resin, synthetic fibers, and the like. Sandwiches of adherent crystal gel/material (i.e. adherent crystal gel-material-adherent crystal gel or material-adherent crystal gel-material, etc.) are ideal for use as shock absorbers, acoustical isolators, vibration dampers, vibration isolators, and wrappers. For example the vibration isolators can be use under research microscopes, office equipment, tables, and the like to remove background vibrations.

Various useful adhesion resins of one or more types can be incorporated in minor amounts into the adherent crystal gel. These include: polymerized mixed olefins, polyterpene, glycerol ester of rosin, pentaerythritol ester of rosin, saturated alicyclic hydrocarbon, coumarone indene, hydrocarbon, mixed olefin, alkylated aromatic hydrocarbon, Polyalphamethylstyrene/vinyl toluene copolymer, polystyrene, special resin, and the like.

The adherent crystal gel compositions of the invention can be casted unto various substrates, such as foam, plastic, fabric, metal, concrete, wood, wire screen, refractory material, glass, synthetic resin, synthetic fibers, and the like, or the adherent crystal gels formed and then can be adhere (attach, cling, fasten, hold, stick) to the desired substrates to form various GnMn, GnGn, GnMnGn, MnGnMn, MnGnGn, GnGnMn, GnGnMn, GnMnMnGn, MnGnGnMn, MnMnGnGn, MnMnMnGnGn, GnMnGnGn, GnMnGnMnMn, MnGnMnGnMnGnMn, or any permutations of said combination composites for uses requiring temporary peel and re-use as well as permanent long-life use as needed. Adhesion to substrates is most desirable when it is necessary to apply the adherent crystal gels to substrates in the absence of heat or on to a low temperature melting point substrate for later peel off after use, such as for sound damping of a adherent crystal gel composite applied to a first surface and later removed for use on a second surface. The low melting substrate materials which can not be exposed to the high heat of the molten adherent crystal gels, such as low melting metals, low melting plastics (polyethylene, PVC, PVE, PVA, and the like) can only be formed by applying the adherent crystal gels to the temperature sensitive substrates. Other low melting plastics include: polyolefins such as polyethylene, polyethylene copolymers, ethylene alpha-olefin resin, ultra low density ethylene-octene-1 copolymers, copolymers of ethylene and hexene, polypropylene, and etc. Other cold applied adherent crystal gels to teflon type polymers: TFE, PTFE, PEA, FEP, etc., polysiloxane as substrates are achieved using the adherent crystal gels of the invention.

Likewise, adherent crystal gel substrate composites can be both formed by casting hot onto a

substrate and then after cooling adhering the opposite side of the adherent crystal gel to a substrate having a low melting point. The adherent crystal gel is most essential when it is not possible to introduce heat in an heat sensitive or explosive environment or in outer space. The use of solid or liquid resins promotes adherent crystal gel adhesion to various substrates both while the adherent crystal gel is applied hot or at room temperature or below or even under water. The adherent crystal gels can be applied without heating to paper, foam, plastic, fabric, metal, concrete, wood, wire screen, refractory material, glass, synthetic resin, synthetic fibers, and the like.

The adhesion properties of the gels are determined by measuring comparable rolling ball tack distance "D" in cm using a standard diameter "d" in mm stainless steel ball rolling off an inclined of height "H" in cm and determining the average force required to perform 180o peel of a heat formed G_1M_1 one inch width sample applied at room temperature to a substrate M_2 to form the composite $M_1G_1M_2$ The peel at a selected standard rate cross-head separation speed of 25 cm/minute at room temperature is initiated at the G_1M_2 interface of the $M_1G_1M_2$ composite, where the substrate M_2 can be any of the substrates mentioned and M_1 preferably a flexible fabric.

Advantageously, glassy phase associating homopolymers such as polystyrene and aromatic resins having low molecular weights of from about 2,500 to about 90,000 can be blended with the triblock copolymers of the invention in large amounts with or without the addition of plasticizer to provide a copolymer-resin alloy of high impact strengths. More advantageously, when blended with multiblock copolymers and substantially random copolymers the impact strengths can be even higher. The impact strength of blends of from about 150 to about 1,500 parts by weight glass phase associating polymer and resins to 100 parts by weight of one or more multiblock copolymers can provide impact strength approaching those of soft metals. At the higher loadings, the impact strength approaches that of polycarbonates of about 12 ft-lb/in notch and higher.

The improvements of the crystal gels of the invention is exceptional, the crystal gels are crystal to the touch and can be quantified using a simple test by taking a freshly cut Crystal gel probe of a selected gel rigidity made from the crystal gels of the invention. The crystal gel probe is a substantially uniform cylindrical shape of length "L" of at least about 3.0 cm formed components (1)-(3) of the crystal gels of the invention in a 16 X 150 mm test tube. The crystal gel probe so formed has a 16 mm diameter hemi-spherical tip which (not unlike the shape of a human finger tip) is brought into perpendicular contact about substantially the center of the top cover of a new, un-touched polystyrene reference surface (for example the top cover surface of a sterile polystyrene petri dish) having a diameter of 100 mm and a weight of 7.6 gram resting on its thin circular edge (which minimizes the vacuum or partial pressure effects of one flat surface in contact with another flat surface) on the flat surface of a scale which scale is tared to zero. The probe's hemi-spherical tip is place in contact with the center of the top of the petri dish cover surface and allowed to remain in contact by the weight of the gel probe while held in the upright position and then lifted up. Observation is made regarding the probe's tackiness with respect to the clean reference polystyrene surface. For purpose of the foregoing reference tack test, tackiness level 0 means the

polystyrene dish cover is not lifted from the scale by the probe and the scale shows substantially an equal positive weight and negative weight swings before settling again back to zero with the swing indicated in (negative) grams being less than 1.0 gram. A tackiness level of one 1, means a negative swing of greater than 1.0 gram but less than 2.0 gram, tackiness level 2, means a negative swing of greater than 2 gram but less than 3 gram, tackiness level 3, means a negative swing of greater than 3 gram but less than 4 gram, before settling back to the zero tared position or reading. Likewise, when the negative weight swing of the scale is greater than the weight of the dish (i.e., for the example referred above, greater than 7.6 gram), then the scale should correctly read -7.6 gram which indicates the dish has completely been lifted off the surface of the scale. Such an event would demonstrate the tackiness of a gel probe having sufficient tack on the probe surface. The crystal gels of the invention fails to lift off the polystyrene reference from the surface of the scale when subject to the foregoing reference tack test. Advantageously, the crystal gels of the invention can register a tackiness level of less than 5, more advantageously, less than 3, still more advantageously, less than 2, and still more advantageously less than 1. The non-tackiness of the crystal gels of the invention can advantageously range from less than 6 to less than 0.5 grams, typical tack levels are less than 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.5, 2.8, 3.0, 3.5, 4.0, 4.5, 5.0 grams and the like. Whereas probes of gels made from amorphous gels such as SEPS, SEBS, S-EP-EB-S, and the like with copolymer styrene to rubber ratio of less than 37:63 and plasticizer of higher than 30 cSt 40oC are found to lift the polystyrene reference from the surface of the scale. For purposes of indicating tack, the method above can provide gel tack level readings of 1, 2, 3, 4, 5, 6, and 7 grams. More accurate and sensitive readings can be made using electronic scales of tack levels of less than 1 gram. By this simple method tack levels (of a gel probe on a polystyrene reference surface) can be measure in terms of gram weight displacement of a scale initially tared to zero. For purpose of the present invention the method of using a polystyrene reference surface having a weight of 7.6 grams in contact and being lifted by the tackiness of a cylindrical gel probe having a 16 mm diameter hemi-spherical tip is used to determine the tackiness of the crystal gels of the invention. The level of tack being measured in gram Tack at 23oC.

The improvements of other properties of the crystal gels over amorphous gels are many, these include: improved damage tolerance, improved crack propagation resistance, improved tear resistance, improved resistance to fatigue, etc. Such crystal gels are advantageous for end-use involving repeated applications of stress and strain resulting from large number of cycles of deformations, including compression, compression-extension (elongation), torsion, torsion-compression, torsion-elongation, tension, tension-compression, tension-torsion, etc. The crystal gels also exhibit improved damage tolerance, crack propagation resistance and especially improved resistance to high stress rupture which combination of properties makes the gels advantageously and surprisingly exceptionally more suitable than amorphous gels made from non-crystalline poly(ethylene) component copolymers at corresponding gel rigidities.

Block copolymers with polyethylene midblocks alone do not form suitable Crystal gels for purpose

of the invention. Crystalline midblock regions needs to be balanced with amorphous midblock regions in order to obtain soft, flexible and elastic gels with the desired crystalline properties that are not found in totally amorphous gels.

The various representative crystalline/glassy domain/amorphous structures of S-E-EB-S, S-E-EB_{25}-S, S-E-EP-E-S, S-EP-E-S and S-EP-E-EP-S. Although the structure are spheroid representation, cylinders and plates are also within the scope of the present invention. Cylinder and plate structure are obtained with increasing glassy A end blocks. From about 15-30% by weight of A blocks, the block copolymer structure is spheroid. From about 33 about 40% by weight of A blocks, the block copolymer structure becomes cylindrical; and above about 45% A blocks, the structure becomes less cylindrical and more plate like.

In order to obtain elastic crystal gels of the invention, it is necessary that the selective synthesis of butadiene produce sufficient amounts of 1,4 poly(butadiene) that on hydrogenation can exhibit "crystallinity" in the midblocks. In order for the block copolymers forming the crystal gels of the invention to exhibit crystallinity, the crystalline midblock segments must contain long runs of -CH2- groups. There should be approximately at least 16 units of -(CH2)- in sequence for crystallinity. Only the (-CH2-)4 units can crystallize, and then only if there are at least 4 units of (-CH2-)4 in sequence; alternatively, the polyethylene units are denoted by [-(CH2-CH2-CH2-CH2)-]4, [(-CH2-)4]4 or (-CH2-)16. The amount of (-CH2-)16 units forming the (E) midblocks of the block copolymers comprising the crystal gels of the invention should be at least about 20% which amount is capable of exhibiting a melting endotherm in differential scanning calorimeter (DSC) curves.

Advantageously, the elastomer midblock segment should have a crystallinity of at least about 20% of (-CH2-)16 units of the total mole % forming the midblocks of the block copolymer, more advantageously at least about 25%, still more advantageously at least about 30%, especially advantageously at least about 40% and especially more advantageously at least about 50% and higher. Broadly, the crystallinity of the midblocks should range from at least about 20% to about 60%, less broadly from at least about 18% to about 65%, and still less broadly from at least 22% to about 70%.

The melting endotherm in DSC curves of the crystalline block copolymers comprising at least 20% crystallinity are much higher than conventional amorphous block copolymers. The poly(ethylene) crystalline segments or midblocks of copolymers forming the crystal gels of the invention are characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 25oC, more advantageously of about 40oC or higher as determined by DSC curve. The maximum in the endotherm curves of the crystalline block copolymers occurs at about 40oC, but can range from greater than about 25oC to about 60oC and higher. The crystalline block copolymers forming the crystal gels of the invention can exhibit melting endotherms (as shown by DSC) of about 25oC to about 75oC and higher. More specific melting endotherm values of the crystalline midblock block copolymers include: about 28oC, 29oC, 30oC, 31oC, 32oC, 33oC, 34oC, 35oC, 36oC, 37oC, 38oC, 39oC, 40oC, 41oC, 42oC, 43oC, 44oC, 45oC, 46oC, 47oC, 48oC, 49oC, 50oC, 51oC, 52oC, 53oC, 54oC, 55oC, 56oC, 57oC, 58oC, 59oC, 60oC, 61oC,

62oC, 63oC, 64oC, 65oC, 66oC, 67oC, 68oC, 69oC, 70oC, 71oC, 72oC, 73oC, 74oC, 75oC, 76oC, 77oC, 78oC, 79oC, 80oC, 90oC, 100oC, 110oC, 120oC, and higher, whereas, the melting endotherm (DSC) for conventional amorphous midblock segment block copolymers are about 10oC and lower.

The melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. Such midblock crystallization endothermic and exothermic characteristics are missing from DSC curves of amorphous gels. The crystallization exotherm and fusion endortherm of the crystalline block copolymer gels of the invention are determined by ASTM D 3417 method.

Generally, the method of obtaining long runs of crystalline -(CH2)- is by sequential block copolymer synthesis followed by hydrogenation. The attainment of crystal gels of the instant invention is solely due to the selective polymerization of the butadiene monomer (forming the midblocks) resulting in one or more predetermined amount of 1,4 poly(butadiene) blocks followed by sequential polymerization of additional midblocks and hydrogenation to produce one or more crystalline midblocks of the final block copolymers.

The crystalline block copolymers are made by sequential block copolymer synthesis, the percentage of crystallinity or (-CH2-)16 units should be at least about (0.67)4 or about 20% and actual crystallinity of about 12%. For example, a selectively synthesized S-EBn-S copolymer having a ratio of 33:67 of 1,2 and 1,4 poly(butadiene) on hydrogenation will result in a midblock with a crystallinity of (0.67)4 or 20%. For sake of simplicity, when n is a subscript of -EB-, n denotes the percentage of (-CH2-)4 units, eg, n = 33 or 20% crystallinity which is the percentage of (0.67)4 or "(-CH2-)16" units. Thus, when n = 28 or 72% of (-CH2-)4 units, the % crystallinity is (0.72)4 or 26.87% crystallinity attributed to (-CH2-)16 units, denoted by -EB_{28}-. As a matter of convention, and for purposes of this specification involving hydrogenated polybutadiene: the notation -E- denotes at least about 85% of (-CH2-)4 units. The notation -B- denotes at least about 70% of [-CH2-CH(C2H5)-] units. The notation -EB- denotes between about 15 and 70% [-CH2-CH(C2H5)-] units. The notation -EBn- denotes n% [-CH2-CH(C2H5)-] units. For hydrogenated polyisoprene: The notation -EP- denotes about at least 90% [-CH2-CH(CH3)-CH2-CH2-] units.

Generally, one or more (E) midblocks can be incorporated at various positions along the midblocks of the block copolymers. Using the sequential process for block copolymer synthesis, The (E) midblocks can be positioned as follows:

a) A-E-W-A
b) A-E-W-E-A
c) A-W-E-W-A
d) A-E-W-E-W-E-W-E-A
e) A-W-E-W-A-E-A-E-W-E-A
f) and etc.

The lower flexibility of block copolymer crystal gels due to (E) midblocks can be balanced by the addition of sequentially (W) midblocks. For example, the sequentially synthesized block copolymer S-E-EB-S can maintain a high degree of flexibility due to the presence of amorphous -EB- block. The sequential block copolymer S-E-EB-B-S can maintain a high degree of flexibility due to the presence of amorphous -EB- and -B- midblocks. The sequential block copolymer S-E-EP-E-S can maintain a high degree of flexibility due to the presence of -EP- midblock. The sequential block copolymer S-E-B-S can maintain a high degree of flexibility due to the presence of the -B- midblock. For S-E-S, where the midblock is substantially crystalline and flexibility low, physical blending with amorphous block copolymers such as S-EB-S, S-B-S, S-EP-S, S-EB-EP-S, (S-EP)n and the like can produce more softer, less rigid, and more flexible crystal gel.

Because of the (E) midblocks, the crystal gels of the invention exhibit different physical characteristics and improvements over substantially amorphous gels including damage tolerance, improved crack propagation resistance, improved tear resistance producing knotty tears as opposed to smooth tears, crystalline melting point of at least 28oC, improved resistance to fatigue, higher hysteresis, etc. Moreover, the crystal gels when stretched exhibit additional yielding as shown by necking caused by stress induced crystallinity. Additionally, the crystallization rates of the crystalline midblocks can be controlled and slowed depending on thermal history producing time delay recovery upon deformation.

Regarding resistance to fatigue, fatigue (as used herein) is the decay of mechanical properties after repeated application of stress and strain. Fatigue tests give information about the ability of a material to resist the development of cracks or crazes resulting from a large number of deformation cycles. Fatigue test can be conducted by subjecting samples of amorphous and crystal gels to deformation cycles to failure (appearance of cracks, crazes, rips or tears in the gels).

Tensile strength can be determined by extending a selected gel sample to break as measured at 180o U bend around a 5.0 mm mandrel attached to a spring scale. Likewise, tear strength of a notched sample can be determined by propagating a tear as measured at 180o U bend around a 5.0 mm diameter mandrel attached to a spring scale.

Various block copolymers can be obtained which are amorphous, highly rubbery, and exhibiting minimum dynamic hysteresis:

Block copolymer S-EB-S

The monomer butadiene can be polymerized in a ether/hydrocarbon solvent to give a 50/50 ratio of 1,2 poly(butadiene)/1,4 poly(butadiene) and on hydrogenation no long runs of -CH2- groups and negligible crystallinity, ie, about $(0.5)^4$ or 0.06 or 6% and actual crystallinity of about 3%. Due to the constraints of Tg and minimum hysteresis, conventional S-EB-S have ethylene-butylene ratios of about 60:40 with a crystallinity of about $(0.6)^4$ or 0.129 or 12% and actual crystallinity of about 7.7%.

Block copolymer S-EP-S

The monomer isoprene when polymerized will produce 95% 1,4 poly(isoprene)/5% 3,4 poly(isoprene) and upon hydrogenation will form amorphous, rubbery poly(ethylene-propylene) midblock and no long runs of -CH2- and no crystallinity.

Mixed block copolymer S-EB/EP-S

The polymerization of a 50/50 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give equal amounts of 1,2 and 1,4 poly(butadiene) on hydrogenation will produce a maximum crystallinity of $(0.25)^4$ or 0.4%. The actual crystallinity would be approximately about 0.2%, which is negligible and results in a good rubbery midblock.

The polymerization of a 80/20 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give equal amounts of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of $(0.10)^4$ or 0.01%. The actual crystallinity would be approximately about 0.006%, which is negligible and results in a good rubbery midblock.

The polymerization of a 20/80 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give equal amounts of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of $(0.4)^4$ or 2.56%. The actual crystallinity would be approximately about 1.53%, which is negligible and results in a good rubbery midblock.

The polymerization of a 20/80 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give a 40:60 ratio of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of (0.48)4 or 5.3%. The actual crystallinity would be approximately about 3.2%, which is negligible and results in a good rubbery midblock.

For purpose of convince and simplicity, the hydrogenated polybutadiene are denoted as follows: -E- denotes at least 85% R-1 units, -B- denotes at least 70% R-2 units, -EB- denotes between 15 and 70% R-2 units, -EBn- denotes n% R-2 units, and -EP- denotes 90% R-3 units.

Table I below gives the % of units on hydrogenation of polybutadiene/polyisoprene copolymer midblocks

|H2

-(CH2)4 -(CH-CH2) ______________ (CH2-CH-CH2-CH2)-(CH2-CH)-

C2H5 CH3 CH

CH3 CH3

n% from polybutadine (1-n)% from polyisoprene

90%•n 10%•n 95%•(1-n) 5%•(1-n)

where n is the mole % polybutadiene in the polybutadiene-polyisoprene starting polymer

n =	R-1	R-2	R-3	R-4
0%	0%	0%	95%	5%
20%	18%	2%	76%	4%
40%	36%	4%	57%	3%
60%	54%	6%	38%	2%
80%	72%	8%	19%	1%
100%	90%	10%	0%	0%

where R-1 denotes (-CH2-)4 ,

R-2 denotes -(CH-CH2)- ,
C2H5

R-3 denotes -(CH2-CH-CH2-CH2)- , and
CH3

R-4 denotes -(CH2-CH)-
CH
CH3 CH3

Therefore, the percentage that can crystallize is [(-CH2-)4]4 since this is the chance of getting four (-CH2-)4 units in sequence. The percentage that will crystallize is about 60% of this.

n =	(-CH2-)4	[(-CH2-)4]4	0.6 X [(-CH2-)4]n
0%	0%	0%	0%
20%	18%	0.1%	0.06%
40%	36%	1.7%	1.0%
60%	54%	8.5%	5.1%
80%	72%	26.9%	16.1%
100%	90%	65.6%	39.4%

This applies to polymerization in a hydrocarbon solvent. In an ether (eg, diethylether), the percentage (-CH2-)4 units will be reduced so that crystallinity will be negligible.

n =	(-CH2-)4	[(-CH2-)4]4	0.6X [(-CH2-)4]n
0%	0%	0%	0%
20%	5%	0.0006%	0.0004%
40%	10%	0.01%	0.006%
60%	15%	0.05%	0.03%
80%	20%	0.16%	0.10%
100%	25%	0.39%	0.23%

These values are all negligible. There will be no detectable crystallinity in any of these polymer midblocks. In a mixed ether/hydrocarbon solvent, values will be intermediate, depending on the ratio of ether to hydrocarbon.

The midblocks (Z) of one or more -E-, -B-, -EB-, or -EP- can comprise various combinations of midblocks between the selected end blocks (A); these include: -E-EB-, -E-EP-, -B-EP-, -B-EB-, -E-EP-E-, -E-EB-B-, -B-EP-B-, -B-EB-B-, -E-B-EB-, -E-B-EP-, -EB-EP-, -E-EB-EP-, -E-EP-EB-, -B-EB-EP-, -B-EP-EB-, -E-EP-E-EP-, -E-EP-E-EB-, -B-EP-B-EP-, -B-EB-B-EB-, -B-EB-B-EP-, -E-EB-B-EP-, -E-EP-B-EB-, -E-EP-E-EP-E-, -B-EP-B-EP-B-, -E-EP-E-EB-, -E-EP-E-EP-EB-, -E-EP-E-EP-E-, -E-EP-EB-EP-EB-B- and the like.

The (i) and (v) block copolymers of (A-Z-A) can be obtained by sequential or random synthesis methods followed by hydrogenation of the midblocks. As denoted above, abbreviations are interchangeably used, for example, (S-E-EP-S) denotes poly(styrene-ethylene-ethylene-co-propylene-styrene). Other linear block copolymers (denoted in abbreviations) include the following: (S-E-EB-S), (S-E-EP-S), (S-B-EP-S), (S-B-EB-S), (S-E-EP-E-S), (S-E-EB-B-S), (S-B-EP-B-S), (S-B-EB-B-S), (S-E-B-EB-S), (S-E-B-EP-S), (S-EB-EP-S), (S-E-EB-EP-S), (S-E-EP-EB-S), (S-B-EB-EP-S), (S-B-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-EP-B-EP-S), (S-B-EB-B-EB-S), (S-B-EB-B-EP-S), (S-E-EB-B-EP-S), (S-E-EP-B-EB-S), (S-E-EP-E-EP-E-S), (S-B-EP-B-EP-B-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-EB-EP-EB-B-S), (S-E-EP-EB-EP-EB..... -S) and the like.

The (ii) and (iv) multiblock star-shaped (or radial) copolymers (A-Z)nX can be obtained by sequential synthesis methods including hydrogenation of selected block copolymers made by polymerizing half of the block copolymers such as SBS or SIS and couple the halves with a coupling agent such as an organic dihalide; or couple with an agent such as SnCl4, which results in star-shaped block copolymers

(four branches). Coupling with divinyl benzene give block copolymers which are very highly branched. Radial block copolymers suitable for use in forming the crystal gels of the present invention include: (S-E-EB-S)n, (S-E-EP)n , (S-B-EP)n, (S-B-EB)n, (S-E-EP-E)n, (S-E-EB-B)n, (S-B-EP-B)n, (S-B-EB-B)n, (S-E-B-EB)n, (S-E-B-EP)n, (S-EB-EP)n, (S-E-EB-EP)n, (S-E-EP-EB)n, (S-B-EB-EP)n, (S-B-EP-EB)n, (S-E-EP-E-EP)n, (S-E-EP-E-EB)n, (S-EP-B-EP)n, (S-B-EB-B-EB)n, (S-B-EB-B-EP)n, (S-E-EB-B-EP)n, (S-E-EP-B-EB)n, (S-E-EP-E-EP-E)n, (S-B-EP-B-EP-B)n, (S-E-EP-E-EB)n, (S-E-EP-E-EP-EB)n, (S-E-EP-E-EP-E)n, (S-E-EP-EB-EP-EB-B)n

The selected amount of crystallinity in the midblock should be sufficient to achieve improvements in one or more physical properties including improved damage tolerance, improved crack propagation resistance, improved tear resistance, improved resistance to fatigue of the bulk gel and resistance to catastrophic fatigue failure of crystal gel composites, such as between the surfaces of the crystal gel and substrate or at the interfaces of the interlocking material(s) and crystal gel, which improvements are not found in amorphous gels at corresponding gel rigidities.

As an example, when fabric interlocked or saturated with amorphous S-EB-S gels (gel composites) are used as gel liners for lower limb or above the knee prosthesis to reduce pain over pressure areas and give relief to the amputee, the commonly used amorphous gels forming the liners can tear or rip apart during marathon racewalk after 50-70 miles. In extended use, the amorphous gels can rip on the bottom of the liner in normal racewalk training of 40-60 miles over a six weeks period. In such demanding applications, the crystal gels are especially advantageous and is found to have greater tear resistance and resistance to fatigue resulting from a large number of deformation cycles than amorphous gels. The crystal gels are also useful for forming various orthotics and prosthetic articles such as for lower extremity prosthesis of the L5664 (lower extremity socket insert, above knee), L5665 (socket insert, multi-durometer, below knee), L5666 (below knee, cuff suspension interface), L5667 (below knee, above knee, socket insert, suction suspension with locking mechanism) type devices as described by the American Orthotic & Prosthetic Association (AOPA) codes. The crystal gels are useful for making AOPA code devices for upper extremity prosthetics. The devices can be cast molded or injection molded in combination with or without fiber or fabric backing or fiber or fabric reinforcement. When such liners are made without fabric backing, various gels can be used to form gel-gel and gel-gel-gel compsites and the like with varying gel rigidities for the different gel layer(s).

Selected linear block and radial copolymers utilized in forming the crystal gels of the invention are characterized as having an ethylene to butylene midblock ratio (E:B) of about 85:15 to about 65:35. Advantageously, the butylene concentration of the midblock is about 35% or less, more advantageously, about 30% or less, still more advantageously, about 25% or less, especially advantageously, about 20% or less. Advantageously, the ethylene to butylene midblock ratios can range from about 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, 70:30, 69:31, 68:32, 67:33, 66:34 to about 65:35.

The A to Z midblock ratio of the block copolymers suitable for forming crystal gels of the invention can range from about 20:80 to 40:60 and higher. More specifically, the values can be 15:85, 19:81, 20:80, 21:79. 22:78. 23:77, 24:76, 25:75, 26:74, 27:73, 28:72, 29:71, 30:70, 31:69, 32:68, 33:67, 34:66, 35:65, 36:64, 37:63, 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49, 52:48, 53:47, 54:46, 55:45, 56:44, 57:43, 58:42, 59:41, 60:40, 61:39, 62:38, 63:37, 64:36, 65:35, 66:34, 6:33, 68:32, 69:31, 70:30 and higher.

The crystal gels can be made in combination with or without a selected amount of one or more selected polymers and copolymers in amounts without substantially decreasing the desired properties. Such polymers includes: thermoplastic crystalline polyurethane elastomers with hydrocarbon blocks, homopolymers, copolymers, block copolymers, polyethylene, polypropylene, polystyrene, polyethylene copolymers, polypropylene copolymers, and the like. Other (vii) polymers and copolymers can be linear, star-shaped (radial), branched, or multiarm; these including: (SBS) styrene-butadiene- styrene block copolymers, (SIS) styrene-isoprene-styrene block copolymers, low and medium viscosity (S-EB-S) styrene-ethylene-butylene- styrene block copolymers, (S-EP) styrene-ethylene-propylene block copolymers, (S-EP-S) styrene-ethylene/propylene-styrene block copolymers, (S-E-EPS) styrene-ethylene-ethylene/propylene-styrene block copolymers, (SB)n styrene-butadiene and (S-EB)n, (S-EB-S)n, (S-E-EP)n, (SEP)n, (SI)n multi-arm, branched or star-shaped copolymers, polyethyleneoxide (EO), poly(dimethylphenylene oxide), teflon (TFE, PTFE, PEA, FEP, etc), optical clear amorphous copolymers based on 2,2-bistrifluoromethyl-4,5-difuoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE), maleated S-EB-S block copolymer, polycarbonate, ethylene vinyl alcohol copolymer, and the like. Still, other polymers include homopolymers which can be utilized in minor amounts; these include: polystyrene, polydimethylsiloxane, polyolefins such as polybutylene, polyethylene, Hoechst Celanese/PEG 20000 UHMW polyethylene (Mw = 1,000,000-6,000,000), polyethylene copolymers, polypropylene, silicone (Tospearl 120A, 145A etc) and the like. Polyurethane thermoplastic crystalline copolymers with hydrocarbon midblocks based on saturated hydrocarbon diols (Handlin, D., Chin. S., and Masse. M., et al. "POLYURETHANE ELASTOMERS BASED ON NEW SATURATED HYDROCARBON DIOLS" Published Society of Plastics Industry, Polyurethane Division, Las Vegas, October 23, 1996) are also suitable for use in blending with the block copolymers (i-vi) used in forming the crystal gels of the invention. Such saturated hydrocarbon diols include hydroxyl terminated oligomers of poly(ethylene-butylene) (EB), poly(ethylene-propylene) (EP),-E-EB-, -E-EP-, -B-EP-, -B-EB-, -E-EP-E-, -E-EB-B-, -B-EP-B-, -B-EB-B-, -E-B-EB-, -E-B-EP-, -EB-EP-, -E-EB-EP-, -E-EP-EB-, -B-EB-EP-, -B-EP-EB-, -E-EP-E-EP-, -E-EP-E-EB-, -B-EP-B-EP-, -B-EB-B-EB-, -B-EB-B-EP-, -E-EB-B-EP-, -E-EP-B-EB-, -E-EP-E-EP-E-, -B-EP-B-EP-B-, -E-EP-E-EB-, -E-EP-E-EP-EB-, -E-EP-E-EP-E-, -E-EP-EB-EP-EB-B- and the like. As an example, thermoplastic polyurethane made with isocyanates and chain extenders such as TMPD and BEPD from saturated hydrocarbon diol KLP L-2203 having a hard segment contents of 22% exhibits clean phase separation of the hard and soft segments with glass a transition of -50oC. KLP L-2203 based TPU's can be mixed with the crystalline block copolymers to form soft crystal gels within

the gel rigidity ranges of the invention.

The high glassy component (viii) copolymers suitable for use in forming the crystal gels of the invention include high styrene component BASF's Styroflex series copolymers including BX 6105 with a statistical SB sequence for the low elastomeric segments (styrene to butadiene ratio of 1:1) and an overall styrene content of almost 70%, high styrene content Shell Kraton G, Kraton D-1122X (SB)n, D-4122 SBS, D-4240 (SB)n, D-4230 (SB)n, DX-1150 SBS, D-4140 SBS, D-1115 SBS, D-4222 SBS, Kraton D-1401P, SEBS, Dexco's Vector 6241-D, 4411-D, Fina's Finaclear high styrene content SBS series copolymers, Phillips Petroleum's XK40 K-Resin styrene/butadiene copolymers, Kuraray's S2104 SEPS. The (viii) copolymers include amorphous polymers with high styrene content: SBS, SIS, SEPS, SEB/EPS, and the like. The (i-viii) copolymers with glassy to elastomeric ratios can range from 37:63, 37.6:62.4, 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49 52:48, 53:47, 54:46, 55:45, 56:44, 57:43, 58:42, 59:41, 60:40, 6:39, 62:38, 63:37, 64:36, 65:35, 66:34, 67:33, 68:32, 69:31, 70:30, 7:29, 72:28, 73:27, 74:26, 75:25, 76:24, 77:23, 78:22, 79:21, to 80:20 and higher.

Suitable polyolefins include polyethylene and polyethylene copolymers such as Dow Chemical Company's Dowlex 3010, 2021D, 2038, 2042A, 2049, 2049A, 2071, 2077, 2244A, 2267A; Dow Affinity ethylene alpha-olefin resin PL-1840, SE-1400, SM-1300; more suitably: Dow Elite 5100, 5110, 5200, 5400, Primacor 141--XT, 1430, 1420, 1320, 3330, 3150, 2912, 3340, 3460; Dow Attane (ultra low density ethylene-octene-1 copolymers) 4803, 4801, 4602, Eastman Mxsten CV copolymers of ethylene and hexene (0.905-0.910 g/cm3).

The conventional term "major" means about 51 weight percent and higher (e.g. 55%, 60%, 65%, 70%, 75%, 80% and the like) and the term "minor" means 49 weight percent and lower (e.g. 2%, 5%, 10%, 15%, 20%, 25% and the like).

Example of polymers, copolymers, and blends include: (a) Kraton G 1651, G 1654X; (b) Kraton G 4600; (c) Kraton G 4609; other suitable high viscosity polymer and oils include: (d) Tuftec H 1051; (e) Tuftec H 1041; (f) Tuftec H 1052; (g) Kuraray SEPS 4033; (h) Kuraray S-EB-S 8006; (i) Kuraray SEPS 2005; (j) Kuraray SEPS 2006 , and (k) blends (polyblends) of (a)-(h) with other polymers and copolymers include: (1) S-EB-S/SBS; (2) S-EB-S/SIS; (3) S-EB-S/(SEP); (4) S-EB-S/(SEB)n; (5) S-EB-S/(SEB)n; (6) S-EB-S/(SEP)n; (7) S-EB-S/(SI)n; (8) S-EB-S/(SI) multiarm; (9) S-EB-S/(SEB)n; (10) (SEB)n star-shaped copolymer; (11) s made from blends of (a)-(k) with other homopolymers include: (12) S-EB-S/polystyrene; (13) S-EB-S/polybutylene; (14) S-EB-S/poly-ethylene; (14) S-EB-S/polypropylene; (16) SEP/S-EB-S, (17) SEP/SEPS, (18) SEP/SEPS/SEB, (19), SEPS/S-EB-S/SEP, (20), SEB/S-EB-S (21), EB-EP/S-EB-S (22), S-EB-S/EB (23), S-EB-S/EP (24), (25) (SEB)n s, (26) (SEP)n, (27) Kuraray 2007 (SEPS), (28) Kuraray 2002, (SEPS), (29) Kuraray 4055 (S-EB-EP-S) (30) Kuraray 4077 (S-EB-EP-S) (31) Kuraray 4045 (S-EB-EP-S) (32) (S-EB-EP)n, (33) (SEB)n, (34) EPDM, (35) EPR, (36) EVA, (37) coPP, (38) EMA, (39) EEA, (40) DuPont Teflon AF amorphous fluoropolymers, (41) Dow polydimethylsiloxane, (42) maleated S-EB-S (maleation level 2-30%), (43) (EP)n and the like.

Septon 4033 (SEEPS), 4045 (SEEPS), 4055 (SEEPS), and 4077 (SEEPS) are made from hydrogenated styrene isoprene/butadiene block copolymers, more specifically from hydrogenated styrene block polymer with 2-methyl-1.3-butadiene and 1,3-butadiene. Corresponding (SEP/EBS) copolymers can be made by proper control of polymerization.

Representative examples of commercial elastomers that can be combined with the block copolymers (i) described above include: Shell Kratons D1101, D1102, D1107, D1111, D1112, D1113X, D1114X, D1116, D1117, D1118X, D1122X, D1125X, D1133X, D1135X, D1184, D1188X, D1300X, D1320X, D4122, D4141, D4158, D4240, G1650, G1652, G1657, G1701X, G1702X, G1726X, G1750X, G1765X, FG1901X, FG1921X, D2103, D2109, D2122X, D3202, D3204, D3226, D5298, D5999X, D7340, G1650, G1651, G1652, G4609, G4600, G1654X, G2701, G2703, G2705, G1706, G2721X, G7155, G7430, G7450, G7523X, G7528X, G7680, G7705, G7702X, G7720, G7722X, G7820, G7821X, G7827, G7890X, G7940, FG1901X and FG1921X. Kuraray's SEP, SEPS, S-EB-S, S-EB-EP-S: Nos. 1001, 1050, 2027, 2003, 2006, 2007, 2008, 2023, 2043, 2063, 2050, 2103, 2104, 2105, 8004, 8006, 8007, H-VS-3 (S-V-EP)n, Dexco polymers (Vector) having high styrene ratios: 4411, 4461, 6241, DPX555, and the like. Septon 2104 has a high styrene content of 65 which is useful for blending with other copolymers to achieve the glassy phase criteria specified above.

The amorphous S-EB-S and (S-EB)n copolymers can have a broad range of styrene to ethylene-butylene ratios (S:EB) of about 20:80 or less to about 40:60 or higher. The S:EB weight ratios can range from lower than about 20:80 to above about 40:60 and higher. More specifically, the values can be 15:85, 19:81, 20:80, 21:79. 22:78. 23:77, 24:76, 25:75, 26:74, 27:73, 28:72, 29:71, 30:70, 31:69, 32:68, 33:67, 34:66, 35:65, 36:64, (and higher ratios for viii copolymers) 37:63, 37.6:62.4, 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49 52:48 and etc. Other ratio values of less than 19:81 or higher than 51:49 are also possible. Broadly, the styrene block to elastomeric block ratio of the high viscosity liner and star copolymers is about 20:80 to about 40:60 or higher, less broadly about 31:69 to about 40:60, preferably about 32:68 to about 38:62, more preferably about 32:68 to about 36:64, particularly more preferably about 32:68 to about 34:66, especially more preferably about 33:67 to about 36:64, and still more preferably about 30:70.

The Brookfield Viscosity of a 5 weight percent solids solution in toluene at 30oC of 2006, 4045, 4055, 4077 typically range about 20-35, about 25-150, about 60-150, about 200-400 respectively. Typical Brookfield Viscosities of a 10 weight percent solids solution in toluene at 30oC of 1001, 1050, 2007, 2063, 2043, 4033, 2005, 2006, are about 70, 70, 17, 29, 32, 50, 1200, and 1220 respectively. Typical Brookfield Viscosity of a 25 weight percent solids solution in toluene at 25oC of Kraton D1101, D1116, D1184, D1300X, G1701X, G1702X are about 4000, 9000, 20000, 6000, 50000 and 50000 cps respectively. Typical Brookfield Viscosity of a 10 weight percent solids solution in toluene at 25oC of G1654X is about 370 cps. The Brookfield Viscosities of a 20 and 30 weight percent solids solution in toluene at 30oC of H-VS-3 are about 133 cps and 350 cps respectively.

Suitable block copolymers and their typical viscosities are further described. Shell Technical

Bulletin SC:1393-92 gives solution viscosity as measured with a Brookfield model RVT viscometer at 25oC for Kraton G 1654X at 10% weight in toluene of approximately 400 cps and at 15% weight in toluene of approximately 5,600 cps. Shell publication SC:68-79 gives solution viscosity at 25oC for Kraton G 1651 at 20 weight percent in toluene of approximately 2,000 cps. When measured at 5 weight percent solution in toluene at 30oC, the solution viscosity of Kraton G 1651 is about 40. Examples of high viscosity S-EB-S triblock copolymers includes Kuraray's S-EB-S 8006 which exhibits a solution viscosity at 5 weight percent at 30oC of about 51 cps. Kuraray's 2006 SEPS polymer exhibits a viscosity at 20 weight percent solution in toluene at 30oC of about 78,000 cps, at 5 weight percent of about 27 cps, at 10 weight percent of about 1220 cps, and at 20 weight percent 78,000 cps. Kuraray SEPS 2005 polymer exhibits a viscosity at 5 weight percent solution in toluene at 30oC of about 28 cps, at 10 weight percent of about 1200 cps, and at 20 weight percent 76,000 cps. Other grades of S-EB-S, SEPS, (SEB)n, (SEP)n polymers can also be utilized in the present invention provided such polymers exhibits the required high viscosity. Such S-EB-S polymers include (high viscosity) Kraton G 1855X which has a Specific Gravity of 0.92, Brookfield Viscosity of a 25 weight percent solids solution in toluene at 25oC of about 40,000 cps or about 8,000 to about 20,000 cps at a 20 weight percent solids solution in toluene at 25oC.

The styrene to ethylene and butylene (S:EB) weight ratios for the Shell designated polymers can have a low range of 20:80 or less. Although the typical ratio values for Kraton G 1651, 4600, and 4609 are approximately about 33:67 and for Kraton G 1855X approximately about 27:73, Kraton G 1654X (a lower molecular weight version of Kraton G 1651 with somewhat lower physical properties such as lower solution and melt viscosity) is approximately about 31:69, these ratios can vary broadly from the typical product specification values. In the case of Kuraray's S-EB-S polymer 8006 the S:EB weight ratio is about 35:65. In the case of Kuraray's 2005 (SEPS), and 2006 (SEPS), the S:EP weight ratios are 20:80 and 35:65 respectively. The styrene to ethylene-ethylene/propylene (S:EB-EP) ratios of Kuraray's SEPTON 4033, 4045, 4055, and 4077 are typically about 30, 37.6, 30, 30 respectively. More typically the (S:EB-EP) and (S:EP) ratios can vary broadly much like S:EB ratios of S-EB-S and (SEB)n from less than 19:81 to higher than 51:49 (as recited above) are possible. It should be noted that multiblock copolymers including SEPTON 4045, 4055, 4077 and the like are described in my cited copending parent applications and are the subject matter of related inventions.

The block copolymers such as Kraton G 1654X having ratios of 31:69 or higher can be used and do exhibit about the same physical properties in many respects to Kraton G 1651 while Kraton G 1654X with ratios below 31:69 can also be use, but they are less advantageous due to their decrease in the desirable properties of the final gel.

Plasticizers particularly advantageous for use in practicing the present invention are will known in the art, they include rubber processing oils such as paraffinic and naphthenic petroleum oils, highly refined aromatic-free paraffinic and naphthenic food and technical grade white petroleum mineral oils, and synthetic liquid oligomers of polybutene, polypropene, polyterpene, etc. The synthetic series process oils

are high viscosity oligomers which are permanently fluid liquid nonolefins, isoparaffins or paraffins of moderate to high molecular weight.

Minor amounts of any compatible plasticizers can be utilized in forming the crystal gels of the invention, but because of the non-tack property of the crystal gels of the invention, the major amount of plasticizers used should be low viscosity plasticizers having viscosities advantageously of not greater than about 30 cSt @ 40oC, for example 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, and the like. Such low viscosity plasticizers are commercially available as, for example, from Witco: Rudol, Ervol, Benol, Blandol, Carnation, Klearol, Semtol100, Semtol 85, Semtol 70, Semtol 40; from Lyondell: Duroprime 55, 70, 90, Durprime DS L & M, Duropac 70, 90, Crystex 22, Crystex AF L & M, Tufflo 6006, 6016 and the like.

Examples of various other representative commercially available plasticizing oils include Amoco® polybutenes, hydrogenated polybutenes, polybutenes with epoxide functionality at one end of the polybutene polymer, liquid poly(ethylene/butylene), liquid hetero-telechelic polymers of poly(ethylene/butylene/styrene) with epoxidized polyisoprene and poly(ethylene/butylene) with epoxidized polyisoprene: Example of such polybutenes include: L-14 (320 Mn), L-50 (420 Mn), L-100 (460 Mn), H-15 (560 Mn), H-25 (610 Mn), H-35 (660 Mn), H-50 (750 Mn), H-100 (920 Mn), H-300 (1290 Mn), L-14E (27-37 cst @ 100oF Viscosity), H-300E (635-690 cst @ 210oF Viscosity), Actipol E6 (365 Mn), E16 (973 Mn), E23 (1433 Mn), Kraton L-2203 and Kraton L-1203, EKP-206, EKP-207, HPVM-2203 and the like. Example of various commercially oils include: ARCO Prime (55, 70, 90, 200, 350, 400 and the like), Duraprime and Tufflo oils (6006, 6016, 6016M, 6026, 6036, 6056, 6206, etc) , other white mineral oils include: Bayol, Bernol, American, Blandol, Drakeol, Ervol, Gloria, Kaydol, Litetek, Lyondell (Duraprime 55, 70, 90, 200, 350, 400, etc), Marcol, Parol, Peneteck, Primol, Protol, Sontex, Witco brand white oils including RR-654-P and the like. Generally, plasticizing oils with average molecular weights less than about 200 and greater than about 700 can also be used (e.g., H-300 (1290 Mn)).

Comparisons of oil extended S-EB-S triblock copolymers have been described in Shell Chemical Company Technical Bulletin SC:1102-89 (April 1989) "KRATON® THERMOPLASTIC RUBBERS IN OIL GELS" which is incorporated herein by reference.

The stearic acid and microcrystalline wax components of the gels described in my earlier US. Patent No. 5760117 are non-sticky, crystal and non-adhering. The non-adhering gels containing additives such as stearic acid and the like, however, feels greasy due the additive's high solubility in oil and low melting points forming a greasy coating on the surface of the gel. The inherently crystal gels which are an improvement over the greasy feeling gels of U. S. Patent No. 5760117 described above, although feels non-adhering and completely non-tacky and non-greasy, can exhibit a high coefficient of friction or high COF.

I have also found that by incorporating sufficient amounts of one or more of a selected (high melting, low oil soluble, and polar) low COF agents (such as polyphenolics with one or more sterically

hindered phenolic hydroxyl groups) in the gels will result in the appearance of large crystals in the interior as well as on the surface of the gels. Such crystals are shown in Fig. 5 (top view) photo of the top of a crystal gel article with phenolic crystals. These crystals have no effect on the high COF of the resulting gels. Contrary to the combined effects of stearic acid and microcrystalline wax, the presence of microcrystalline wax with polyphenolic in gels does not lessen the gel's COF and have little effect on reducing the size of the large polyphenolic crystals. Likewise the crystallinity and glassy components by themselves can not by themselves reduce the inherent high COF of these gels. Consequently, gels containing microcrystalline wax and polyphenolics exhibit high COF.

Surprisingly, when selected amounts of internal nucleating agents are incorporated in the gels in combination with selected amounts of one or more of a low COF agents, the large crystals no longer forms within the gels; and the surface of the gels exhibit lower and lower COF with time. Bringing the gels in contact with selected external nucleating agents decreases the time or totally eliminates the time needed for the gel's outer surface to exhibit a low COF.

The gels and soft elastomers incorporating low COF agents and internal and/or external nucleating agents exhibit a much lower coefficient of friction when measured in contact with a reference surface than gels and soft elastomers made without such components.

School book physics teaches COF can be determined experimentally, for two given surfaces that are dry and not lubricated, the ratio of the tangential force needed to overcome the friction to the normal force which holds the two surfaces in contact (e.g., the weight of a block of gel or elastomer material on a surface) is a constant, independent of the area or of the velocity with which the surfaces (surface of a side of the block in contact with another surface) move over wide limits. This ratio is μ, the coefficient of friction. The coefficient of sliding friction for a block of material being

$$\mu = (f/F_n)$$

where f is the force of friction, and F_n the normal force. For the case of the block on the horizontal table, if m is the mass of the block, then mg is the normal force and the above equation can be written as

$$\mu = f/mg.$$

In the case the block of a block rests on a board, originally horizontal, and that the board then is tilted until a limiting angle ø is reached, beyond which the block will begin to slide down the board. At this angle the component of the weight of the object along the board is just equal in amount to that necessary to overcome the force of friction. The force down the plane is mg sin ø, while the normal force is mg cos ø. Therefore we have

$$\mu = (mg \sin \phi)/(mg \cos \phi) \text{ or } \mu = \tan \phi.$$

The limiting value of ø for which $\mu = \tan ø$ is true is call the angle of repose. Measurement of the tangent of this angle will give the coefficient of friction of the contacting surfaces of the block and the board that slide one upon the other.

As an example of low COF agents advantageously useful in soft thermoplastic elastomers and gels, excellent results is achieved with 50 grams of a polyphenolic with sterically hindered phenolic hydroxyl groups (Irganox 1010), about 100 grams of one or more nucleating agents (such as very fine particle size sodium benzoate, dibenzylidene sorbitol, its alkylated derivatives, talc, zinc stearate, amorphous silica, aluminum stearate, etc.) and 5,000 grams of S-EB-S and 25,000 gram of oil. The same excellent result is achieved when S-EB-S is adjusted to 3,000 grams, 4,000 grams, etc. The same result is achieved with copolymers as well as in combination with other polymers. Moreover, when about 50 grams of tetrakis[methylene 3,-(3'5'-di-tertbutyl-4"-hydroxyphenyl) propionate] methane is use (per about 22.68 Kilograms or 50 lbs of gel) as a low COF agent, tack is completely removed from the surface of the gel after two to three weeks of blooming.

When this is repeated with an external nucleating agent, such as with various fine particles for coating the outside surface of the elastomer or gel, such as with talc, calcium stearate, zinc stearate, amorphous silica, aluminum stearate, fine flour, corn starch, fine soil, fine sand, fine metallic powder, vacuum dust, fine wood dusts and the like, lower COF is achieved within a few days to less than several hours. After coating the gel for the desired period of time, the fine polar and water soluble particles can be washed off with water and soap, while non-polar and non-water soluble fine powders can be removed by wearing it off or by lifting it off with the use of adhesive tapes if so desired. Fig. 6. (top view) photo of the top of a crystal gel article made with phenolics and external nucleating agents.

What is the surface properties of low CFO agents at the air/plasticizer-copolymer interface? Theory notwithstanding, the resulting gel surface will comprise of very fine molecular segments or even very fine crystal grains of low COF agents confined at the air/plasticizer and polymer interface. Depending on concentration, the non-polar segments of the low COF agents will have a tendency of being adsorpted by the predominate plasticizer and copolymer midblock phase at the gel surface. The slightly polar or more polar segments of the low COF agents are adsorbed to a lesser extent by the plasticizer-copolymer surface. This is supported by observing the water wetting characteristics at the gel surface with and with out low COF agents at the air gel surface interface. A drop of water will bead up and not readily wet the gel surface free of any low COF agents (hydrophobic). The presence of even slightly polar low COF agents exposed on the surface of the gel will make a drop of water flatten out and not bead up when place on the gel surface (hydrophilic).

Commercial high melting point, low oil solubility, and polar low COF agents such as polyphenolics which are advantageously useful in the present invention include: Ethanox 330 (Ethyl), Irganox 1010 (Ciba-Geigy), Santechhem A/O 15-1 (Santech), Ultra 210 (GE), Hostanox 03 (Hoechst Celanese), Irganox 3114 (Ciba-Geigy), Mixxim AO-3 (Fairmont), and the like. Other high melting point, low oil solubility, polar low COF agents contemplated are common amino acids: Such As Alamine,

Arginine, Asparagine, Aspartic Acid, Cysteine, Glutamine, Glutamic Acid, Glycine, Histidine, Isoleucine, Leucine, Lysine, Methionine, Phenylalanine, Proline, Serine, Threonine, Tryptophan, Tyrosine and Valine. The melting points of these amino acids range from about 178oC to about 344oC. The amino acids having greater advantage serving as low COF agents are Asparagine, Aspartic acid. Glutamine, Glutamic acid, Tryptophan, and Tyrosine

Copolymer for forming the low COF compositions include block copolymers, random copolymers, metallocene catalyzed ethylene-styrene copolymers, Low COF crystal gels made from thermoplastic elastomer copolymers and block copolymers having one or more substantially crystalline polyethylene segments or midblocks. The low COF crystal gels advantageously exhibit high, higher, and higher, and ever higher tear resistance than realized before as well as improved high tensile strength. The low COF crystal gels also exhibit improved damage tolerance, crack propagation resistance and especially improved resistance to high stress rupture which combination of properties makes the gels advantageously and surprisingly suitable for use as toys, inflatable air cushions in automobiles, and the like.

The crystal gels of this invention are advantageously useful for making low COF gel compositions. Moreover, various polymer gels made from linear triblock copolymers, multi-arm block copolymers, branched block copolymers, radial block copolymers, multiblock copolymers, random/non-random copolymers, thermoplastic crystalline polyurethane copolymers with hydrocarbon midblocks or mixtures of two or more of such copolymers can also be made with low COF. The COF values of the crystal gels formed form the low COF and nucleating agents are found to be about less than 1, more advantageously less than 0.7, more advantageously less than 0.577, still more advantageously less than 0.466 and still more advantageously less tan 0.40. The low COF crystal gels of the invention can range from less than 1.0 to about less than 0.40.

The crystal gels can also contain useful amounts of conventionally employed additives such as stabilizers, antioxidants, antiblocking agents, colorants, fragrances, flame retardants, flavors, other polymers in minor amounts and the like to an extend not affecting or substantially decreasing the desired properties. Additives useful in the crystal gel of the present invention include: tetrakis[methylene 3,-(3'5'-di-tertbutyl-4"-hydroxyphenyl) propionate] methane, octadecyl 3-(3",5"-di-tert-butyl-4"-hydroxyphenyl) propionate, distearyl-pentaerythritol-diproprionate, thiodiethylene bis-(3,5-ter-butyl-4-hydroxy) hydrocinnamate, (1,3,5-trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl] benzene), 4,4"-methylenebis(2,6-di-tert-butylphenol), stearic acid, oleic acid, stearamide, behenamide, oleamide, erucamide, N,N"-ethylenebisstearamide, N,N"-ethylenebisoleamide, sterryl erucamide, erucyl erucamide, oleyl palmitamide, stearyl stearamide, erucyl stearamide, calcium stearate, other metal sterates, waxes (e.g., polyethylene, polypropylene, microcrystalline, carnauba, paraffin, montan, candelilla, beeswax, ozokerite, ceresine, and the like), teflon (TFE, PTFE, PEA, FEP, etc), polysiloxane, etc. The crystal gel can also contain metallic pigments (aluminum and brass flakes), TiO2, mica, fluorescent dyes and pigments, phosphorescent pigments, aluminatrihydrate, antimony oxide, iron oxides (Fe3O4, -Fe2O3, etc.), iron cobalt oxides, chromium dioxide, iron, barium ferrite, strontium ferrite and other magnetic

particle materials, molybdenum, silicones, silicone fluids, lake pigments, aluminates, ceramic pigments, ironblues, ultramarines, phthalocynines, azo pigments, carbon blacks, silicon dioxide, silica, clay, feldspar, glass microspheres, barium ferrite, wollastonite and the like. The report of the committee on Magnetic Materials, Publication NMAB-426, National Academy Press (1985) is incorporated herein by reference.

The crystal gels can also be made into composites. The crystal gels can be casted unto various substrates, such as open cell materials, metals, ceramics, glasses, and plastics, elastomers, fluropolymers, expanded fluropolymers, Teflon (TFE, PTFE, PEA, FEP, etc), expanded Teflon, spongy expanded nylon, etc.; the molten crystal gel is deformed as it is being cooled. Useful open-cell plastics include: polyamides, polyimides, polyesters, polyisocyanurates, polyisocyanates, polyurethanes, poly(vinyl alcohol), etc. Suitable open-celled Plastic (sponges) are described in "Expanded Plastics and Related Products", Chemical Technology Review No. 221, Noyes Data Corp., 1983, and " Applied Polymer Science", Organic Coatings and Plastic Chemistry, 1975. These publications are incorporated herein by reference.

The crystal gels denoted as “G” can be physically interlocked with a selected material denoted as “M” to form composites as denoted for simplicity by their combinations GnGn, GnGnGn, GnMn, GnMnGn, MnGnMn, MnGnGn, GnGnMn, MnMnMnGn, MnMnMnGnMn, MnGnGnMn, GnMnGnGn, GnMnMnGn, GnMnMnGn, GnGnMn Mn, GnGnMn GnMn, GnMnGnGn, GnGnMn, GnMnGnMnMn, MnGnMnGnMnGn, GnGnMnMnGn, GnGnMnGnMnGn, and the like or any of their permutations of one or more Gn with Mn and the like, wherein when n is a subscript of M, n is the same or different selected from the group consisting of paper, foam, plastic, fabric, metal, concrete, wood, glass, ceramics, synthetic resin, synthetic fibers or refractory materials and the like; wherein when n is a subscript of G, n denotes the same or a different gel rigidity of from about 2 gram to about 1,800 gram Bloom). The crystal gels of the composites are formed from copolymers, polymers, and plasticizers described above.

Sandwiches of crystal gel-material (i.e., crystal gel-material- crystal gel or material-crystal gel-material, etc.) are useful as dental floss, shock absorbers, acoustical isolators, vibration dampers, vibration isolators, and wrappers. For example the vibration isolators can be use under research microscopes, office equipment, tables, and the like to remove background vibrations. The tear resistance nature of the instant crystal gels are superior in performance to amorphous block copolymer gels which are much less resistance to crack propagation caused by long term continue dynamic loadings.

The crystal gels are prepared by blending together the components including other additatives as desired at about 23oC to about 100oC forming a paste like mixture and further heating said mixture uniformly to about 150oC to about 200oC until a homogeneous molten blend is obtained. Lower and higher temperatures can also be utilized depending on the viscosity of the oils and amounts of multiblock copolymers and polymer used. These components blend easily in the melt and a heated vessel equipped with a stirrer is all that is required. Small batches can be easily blended in a test tube using a glass stirring rod for mixing. While conventional large vessels with pressure and/or vacuum means can be utilized in

forming large batches of the instant crystal gels in amounts of about 40 lbs or less to 10,000 lbs or more. For example, in a large vessel, inert gases can be employed for removing the composition from a closed vessel at the end of mixing and a partial vacuum can be applied to remove any entrapped bubbles. Stirring rates utilized for large batches can range from about less than 10 rpm to about 40 rpm or higher.

The crystal gel articles can be formed by blending, injection molding, extruding, spinning, casting, dipping and other conventional methods. For example, Shapes having various cross-section can be extruded. The crystal gels can also be formed directly into articles or remelted in any suitable hot melt applicator and extruded into shaped articles and films or spun into threads, strips, bands, yarns, or other shapes. With respect to various shapes and yarn, its size are conventionally measured in denier (grams/9000 meter), tex (grams/1000 meter), and gage (1/2.54 cm). Gage, tex, denier can be converted as follows: tex = denier/9 = specific gravity (2135/gage), for rectangular cross section, tex = specific gravity (5806 X 103)(th)(w)/9, where th is the thickness and w the width of the strip, both in centimeters. General descriptions of (1) block copolymers, (2) elastomeric fibers and conventional (3) gels are found in volume 2, starting at pp. 324-415, volume 6, pp 733-755, and volume 7, pp. 515 of ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, 1987 which volumes are incorporated herein by reference.

The crystal gels are excellent for cast molding and the molded products have various excellent characteristics which cannot be anticipated form the properties of the raw components. Other conventional methods of forming the composition can be utilized.

Not only do the crystal gels have all the desirable combination of physical and mechanical properties substantially similar to high viscosity amorphous S-EB-S gels such as high elongation at break of at least 1,600%, ultimate tensile strength of about 8X105 dyne/cm2 and higher, low elongation set at break of substantially not greater than about 2%, substantially about 100% snap back when extended to 1,200% elongation, and a gel rigidity of substantially from about 2 gram to about 1,800 gram Bloom and higher, the crystal gels of the present invention exhibit improved tear resistance and resistance to fatigue not obtainable from amorphous S-EB-S gels at corresponding gel rigidities.

The crystal gels of the present invention exhibit one or more of the following properties. These are: (1) tensile strength of about 8X105 dyne/cm2 to about 107 dyne/cm2 and greater; (2) elongation of less than about 1,600% to about 3,000% and higher; (3) elasticity modules of about 104 dyne/cm2 to about 106 dyne/cm2 and greater; (4) shear modules of about 104 dyne/cm2 to about 106 dyne/cm2 and greater as measured with a 1, 2, and 3 kilogram load at 23oC; (5) gel rigidity of about less than about 2 gram Bloom to about 1,800 gram Bloom and higher as measured by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square cm at 23oC; (6) tear propagation resistance greater than the tear resistance of amorphous S-EB-S gels at corresponding gel rigidities; (7) resistance to fatigue greater than the fatigue resistance of amorphous S-EB-S gels at corresponding gel rigidities; (8) and substantially 100% snap back recovery when extended at a crosshead separation speed of 25 cm/minute to 1,200% at 23oC. Properties (1), (2), (3), and (6) above are measured at a crosshead separation speed of 25 cm/minute at 23oC.

The crystal gel articles molded from the instant crystal gels have additional important advantages in that they end-use performance properties are greater than amorphous S-EB-S gels in that they are more resistant to cracking, tearing, crazing or rupture in flexural, tension, compression, or other deforming conditions of use. Like amorphous gels, the molded articles made from the instant composition possess the intrinsic properties of elastic memory enabling the articles to recover and retain its original molded shape after many extreme deformation cycles.

Because of their improved tear resistance and improved resistance to fatigue, the crystal gels of the present invention achieve greater performance than amorphous gels in low frequency vibration applications, such as viscoelastic layers in constrained-layer damping of mechanical structures and goods, as viscoelastic layers used in laminates for isolation of acoustical and mechanical noise, as anti-vibration elastic support for transporting shock sensitive loads, as vibration isolators for an optical table, as viscoelastic layers used in wrappings, enclosures and linings to control sound, as compositions for use in shock and dielectric encapsulation of optical, electrical, and electronic components.

Because of their improved tear resistance and improved resistance to fatigue, the crystal gels are more useful as molded shape articles for use in medical and sport health care, such use include therapeutic hand exercising grips, dental floss, crutch cushions, cervical pillows, bed wedge pillows, leg rest, neck cushion, mattress, bed pads, elbow padding, dermal pads, wheelchair cushions, helmet liner, cold and hot packs, exercise weight belts, traction pads and belts, cushions for splints, slings, and braces (for the hand, wrist, finger, forearm, knee, leg, clavicle, shoulder, foot, ankle, neck, back, rib, etc.), and also soles for orthopedic shoes. Other uses include various shaped articles, optical uses (e.g., cladding for cushioning optical fibers from bending stresses) and various optical devices, as lint removers, dental floss, as tips for swabs, as fishing bate, as a high vacuum seal (against atmosphere pressure) which contains a useful amount of a mineral oil-based magnetic fluid particles, etc. Moreover, the casted, extruded, or spun threads, strips, yarns, tapes can be weaved into cloths, fine or coarse fabrics. The forms of the crystal gel yarn can be bare, double-covered, single-covered or coreplied, and core-spun. The crystal gels can also be made into fibers such as side-side fibers, sheath-core fibers, multiple-segment fibers, island-in-the-sea fibers, and matrix-fibril.

The weaved crystal gels are of great advantage for forming orthotics and prosthetic articles described above because such devices made from weaved crystal gels of fine to coarse fabrics will allow for the human skin to breathe. The openings between weaved strands allows for air and oxygen transport between the skin and outer portions of the gel device body. Moreover, fine oriented or non-oriented crystal gels (made from SEEBS, SEEPS, E-S-E, SEEPES, SEPEEPS and the like) in the form of threads or yarns can be produced by extruding, spinning or forced through a collection of jet nozzles to form a crystal gel spray to produce porous gel non-woven matting or webs which are skin oxygen/air breathe-able fabrics and articles. Unlike the elastomeric nonwoven webs made at 290oC of U.S. Patent 4,692,371, the crystal gels must be formed advantageously below 180oC, more advantageously at about 175oC or lower because of the extremely high amount of plasticizer components. If the crystal gels are heated to above

200oC and higher, the result is a puddle of hot liquid gel mass and not the porous individual form strands forming the desired fabrics. Furthermore, the crystal gels are superior in properties than any gels made from amorphous SEBS gels of substantially corresponding rigidities.

Porous, webbing or matting that are skin breathe-able comprising crystal gel strands can be formed into a webs or matting by cold forming sandwiched crystal gels strand-composites using alkyl cyanoacrylates such as ethyl, butyl, methyl, propyl cyanoacrylates and the like. The alkyl cyanoacrylates (AC) will interlock with the gels of the invention, thereby resulting in gel-(AC)-gel composite webbing or matting articles. Alkyl cyanoacrylates are useful for interlocking crystal gels of the invention with other substrates such as pottery, porcelain, wood, metal, plastics, such as acrylics, ABS, EPDM, nylon Fiberglass, phenoics, plexiglass, polycarbonate, polyesters, polystyrene, PVC, urethanes and the like. Other cyanoacrylates such as cyanoacrylate ester are inhibited interlocking with the crystal gels of the invention.

The crystal gels can be formed in any shape; the original shape can be deformed into another shape (to contact a regular or irregular surface) by pressure and upon removal of the applied pressure, the composition in the deformed shape will recover back to its original shape.

As an example of the versatility of use of the instant crystal gels, a hand exerciser can be made in any shape so long as it is suitable for use as a hand exerciser: a sphere shape, a cube shape, a rectangular shape, etc. Likewise, a wheelchair cushion can be made from the composition in any shape, so long as it meets the needs of the user of the cushion. For example, a cushion can be made by forming the composition into a selected shape matching the contours of the specific body part or body region. The composition can be formed into any desired shaped, size and thickness suitable as a cushion; the shaped composition can be additionally surrounded with film, fabric, foam, or any other desired material or combinations thereof. Moreover, the composition can be casted onto such materials, provided such materials substantially maintain their integrity (shape, appearance, texture, etc.) during the casting process. The same applies for brace cushions, liners, linings and protective coverings for the hand, wrist, finger, forearm, knee, leg, etc.

Because of their improved tear resistance and resistance to fatigue, the crystal gels exhibit versatility as balloons for medical uses, such as balloon for valvuloplasty of the mitral valve, gastrointestinal balloon dilator, esophageal balloon dilator, dilating balloon catheter use in coronary angiogram and the like. Since the crystal gels are more tear resistant, they are especially useful for making condoms, toy balloons, and surgical and examination gloves. As toy balloons, the crystal gels are safer because it will not rupture or explode when punctured as would latex balloons which often times cause injures or death to children by choking from pieces of latex rubber. The crystal gels are advantageously useful for making gloves, thin gloves for surgery and examination and thicker gloves for vibration damping which prevents damage to blood capillaries in the fingers and hand caused by handling strong shock and vibrating equipment.

Other uses include self sealing enclosures for splicing electrical and telephone cables and wires. For example, the crystal gels can be pre-formed into a small diameter tubing within an outer elastic tubing, both the internal crystal gel tubing and external elastic tubing can be axially expanded and fixed in place by a removable continuous retainer. Upon insertion of a spliced pair or bundle of cables or wires, the retainer can be removed, as the retainer is removed, the crystal gel and elastic tubing impinges onto the inserted cables or wires splices, thereby sealing the electrical splices against weather, water, dirt, corrosives and shielding the splice from external abuse. The enclosure is completed without the use of heat or flame as is conventionally performed.

Because of their improved resistance to tearing, the crystal gels do not tear as readily as amorphous gels when used as dental floss. The dental floss can be almost any shape so long as it is suitable for dental flossing. A thick shaped piece of the composition can be stretched into a thin shape and used for flossing. A thinner shaped piece would require less stretching, etc. For purposes of dental flossing, while flossing between two closely adjacent teeth, especially between two adjacent teeth with substantial contact points and more especially between two adjacent teeth with substantial amalgam alloy metal contact points showing no gap between the teeth, it is critical that the crystal gel resist tearing, shearing, and crazing while being stretched to a high degree in such situations. For example, dental crystal gel floss can take the form of a disk where the segments of the circumference of the disk is stretched for flossing between the teeth. Other shaped articles suitable for flossing include threads, strips, yarns, tapes, etc., mentioned above.

In order for crystal gels to be useful as a dental floss, it must overcome the difficult barriers of high shearing and high tearing under extreme elongation and tension loads. The difficulties that the crystal gels must overcome during flossing can be viewed as follows: during the action of flossing, the crystal gel is stretched from no less than about 200% to about 1,100% or higher, the crystal gel floss is deformed as it is pulled down with tearing action between the contacting surfaces of the teeth, then, the wedge of crystal gel floss is sheared between the inner contacting surfaces of the teeth, and finally, the elongated wedged of crystal gel floss is pulled upwards and out between the surfaces of the teeth. The forces encountered in the act of flossing are: tension, shearing, tearing under extreme tension.

The use of crystal gels advances the flossing art by providing strong, soft, and more tear resistant gels than amorphous gels. Floss made from the crystal gels has many advantages over conventional dental floss such as regular and extra fine waxed and unwaxed nylon floss, spongy nylon fiber floss, and waxed and unwaxed expanded and unexpended teflon floss. Such conventional floss are not recommended for use by children, since a slip or sudden snap in forcing the floss between the teeth can cause injury to the gums which often times results in bleeding. For sensitive gums and inflamed gums which has become red and puffy, it is difficult to floss at, near, and below the gumline. The soft crystal gel floss with softness substantially matching the softness of the gums are of great advantage for use by children and for flossing teeth surrounded by sensitive and tender gums.

In all cases, the tear strength of crystal gels are higher than that of amorphous gels. The rigidities

of the crystal gels for use as dental floss advantageously should be selected to exhibit a propagating tear force (when propagating a tear as measured at 180o U bend around a 5.0 mm diameter mandrel attached to a spring scale) of at least about 1 Kg/cm, more advantageously at least 2 Kg/cm, and still more advantageously of about 3 Kg/cm and higher. For any gel to be considered useful for flossing, the gels should exhibit tear strengths of at least 2 Kg/cm'and higher, advantageously of at least 4 Kg/cm and higher, more advantageously of at least 6 Kg/cm and higher, exceptionally more advantageously of at least 8 Kg/cm and higher. Typically, the tear propagation strength should range from about 5 Kg/cm to about 20 Kg/cm and higher, more typically from about less than 5 Kg/cm to about 25 Kg/cm and higher, especially more typically form about less than 6 Kg/cm to about 30 Kg/cm and higher, and exceptionally more typically from about less than 8 Kg/cm to about 35 Kg/cm and higher.

For any gel to be considered useful for flossing, the gels, critically, should advantageously exhibit a propagating tension tear force (when a cylindrical sample is notched and a tear is initiated at the notched area and propagated past its maximum cylindrical diameter by length-wise stretching of the cylindrical sample) of at least about 1 Kg/cm, more advantageously at least 2 Kg/cm, and still more advantageously of about 4 Kg/cm and higher. Although the crystal gels of the present invention have improved tear resistance and resistance to fatigue greater than the amorphous gels at corresponding gel rigidities, the high and ultra-high tear resistant gels of my other related parent and c-i-p applications typically will exhibit even higher tear resistance values.

The crystal gels of the invention can be use for making air bags. The expansion of the gel air bag is substantially pure volume expansion or dilation as related to K, bulk modulus, y, young's modulus: K=y/3(1-2t), t=3k-2n/6k-2n, where t=poisson's ratio, b=1/k compressibility = -change in V/(V• change in pressure P).

Surface expansion measure of air bag from initial to expanded state is from 630 to 833% depending on thickness of original air bag. The initial air bag thickness can vary from .5 cm to 10 cms. (.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 cm and higher).

While advantageous components and formulation ranges based on the desired properties of the crystal gels have been disclosed herein. Persons of skill in the art can extend these ranges using appropriate material according to the principles discussed herein. All such variations and deviations which rely on the teachings through which the present invention has advanced the art are considered to be within the spirit and scope of the present invention.

The invention is further illustrated by means of the following illustrative embodiments, which are given for purpose of illustration only and are not meant to limit the invention to the particular components and amounts disclosed.

EXAMPLE I

Gels of 100 parts of Kraton G1651, Kraton RP-6917 (amorphous S-EB-S), Septon 8006 (amorphous S-EB-S), Kraton RP-6918, Septon S2006 (amorphous S-EP-S) and a high viscosity radial

amorphous midblock segment (SEB)n triblock copolymers and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer having Vis. cSt @ 40oC of 39.0) are melt blended, test, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the tensile strength, notched tear strength, and resistance to fatigue are found to decrease with increase amounts of plasticizers, while tackiness of the gels is found to be greater than 7.6 gram Tack.

EXAMPLE II

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer having Vis. cSt @ 40oC of 39.0) are melt blended, test and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the gel tackiness are found to increase with increase amounts of plasticizers and the tack greater than 7.6 gram Tack.

EXAMPLE III

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow S series poly(ethylene/styrene) random copolymer (250,000 Mw) having a high styrene content sufficient to form gel blends with total styrene content of 37 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE IV

Gels of 100 parts of Septon 4045 (crystalline S-E/EP-S having a styrene content of 37.6) and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime Klearol white oil (plasticizer having Vis. CSt @ 40oC of 7-10) are melt blended, test and probe samples molded, the bulk gel rigidities are found to be within the range of 2 to 2,000 gram Bloom and the tackiness is found to be less than about 1 gram Tack.

EXAMPLE V

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of Septon 2104 (Amorphous SEPS having a high styrene content of 65) and 800,

600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE VI

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow M series poly(ethylene/styrene) random copolymer (350,000 Mw) having a high styrene content sufficient to form gel blends with total styrene content of 37 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE VII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow E series poly(ethylene/styrene) random copolymer (240,000 Mw) having a high styrene content sufficient to form gel blends with total styrene content of 37 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE VIII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with polystyrene homopolymers (having Mw of 3,000; 4,000; 5,000; 6,000; 7,000; 8,000; 9,000; 10,000; 11,000; 12,000, 13,000; 14,000; 15,000; 16,000; 17,000; 18,000; 19,000; 20,000; 30,000; 40,000; 50,000; 60,000; 70,000; 80,000; 90,000) in sufficient amounts to form gel blends with total styrene content of 37, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40

(plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 2,000 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE IX

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow M series poly(ethylene/styrene) random copolymer (350,000 Mw) having a high styrene content sufficient to form gel blends with total styrene contents of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE X

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow S series poly(ethylene/styrene) random copolymers (with Mw of 140,000; 250,000 and 340,000) having a high styrene content sufficient to form gel blends with total styrene content of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XI

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow E series poly(ethylene/styrene) random copolymers (with Mw of 250,000; 340,000 and 400,000) having a high styrene content sufficient to form gel blends with total styrene content of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the

notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow M series poly(ethylene/styrene) random copolymer (with Mw of 250,000; 340,000 and 400,000) having a high styrene content sufficient to form gel blends with total styrene content of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XIII

Gels of 100 parts of Dow E series crystalline poly(ethylene/styrene) random copolymer (with Mw of 250,000; 340,000 and 400,000) having a high styrene content sufficient to form gel blends with total styrene content of 37, 40, 45, 48, 50, 55, and 60 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XIV

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with polystyrene (of 2,500 Mw, 4,000 Mw, 13,000 Mw, 20,000 Mw, 35,000 Mw, 50,000 Mw, and 90,000 Mw; poly(alpha-methylstyrene) (of 1,300 Mw, 4,000 Mw; poly(4-methylstyrene)(of 72,000 Mw), Endex 155, 160, Kristalex 120, and 140) in sufficient amounts to form gel blends with total styrene content of 37, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 2,000 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XV

Examples XIV is repeated and gels of 100 parts of (S-EB_{45}-EP-S), (S-E-EB_{25}-S), (S-EP-E-EP-S), (S-E-EB-S), (S-E-EP-S), (S-E-EP-E-S), (S-E-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), and (S-E-EP-E-EP-E-S) block copolymers are each melt blended, tests and probe samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XVI

Example XIV is repeated and minor amounts of 2, 5, 10 and 15 parts of the following polymers are formulated with each of the triblock copolymers: styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, low viscosity styrene-ethylene-butylene-styrene block copolymers, styrene-ethylene-propylene block copolymers, styrene-ethylene-propylene-styrene block copolymers, styrene-butadiene, styrene-isoprene, polyethyleneoxide, poly(dimethylphenylene oxide), polystyrene, polybutylene, polyethylene, polypropylene, high ethylene content EPDM, amorphous copolymers based on 2,2-bistrifluoromethyl-4,5-difuoro-1,3-dioxole/tetrafluoroethylene. The bulk gel rigidities of each of the formulations are found to be within the range of 2 gram to 2,000 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XVII

Molten gels of Examples III-XVI are formed into composites with paper, foam, plastic, elastomers, fabric, metal, concrete, wood, glass, ceramics, synthetic resin, synthetic fibers, and refractory materials and the resistance to fatigue of the composite-crystal gels at corresponding rigidities are found to be greater than that of the composite-amorphous gels of Example I.

EXAMPLE XVIII

Three cm thick sheets of each of the crystal gels of Example XIV and the amorphous gels of Example I are tested by repeatedly displacing the sheets to a depth of 1 cm using a 10 cm diameter smooth (water soaked) wood plunger for 1,000, 5,000, 10,000, 25,000, 50,000, and 100,000 cycles. The sheets of crystal gels are found capable of exhibiting greater fatigue resistance than the sheets of amorphous gels at corresponding rigidities.

EXAMPLE XIX

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES16 having 37.5% crystallinity and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation,

Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XX

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES24 having 26.6% crystallinity and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXI

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES27 having 17.4% crystallinity and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES28 having 22.9% crystallinity and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXIII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES30 having 19.6% crystallinity and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt

blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXIV

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES44 having 5.0% crystallinity and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXV

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES72 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXVI

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES73 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXVII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES74 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom

and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXVIII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES69 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXIX

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES62 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXX

Gels of 100 parts of Septon (SEPS) copolymers Kraton GRP6918 in combination with each of a Dow poly(ethylene/styrene) random copolymers ES16, ES24, ES27, ES28, ES30, and ES44 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXXI

Gels of 100 parts of Septon (SEBS) copolymers S8006 and Kraton G1651, G1654 in combination with sufficient amounts of a Dow poly(ethylene/styrene) random copolymers ES16, ES24, ES27, ES28, ES30, and ES44 and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXXII

Gels of 100 parts of Septon (SEEPS) copolymers 4033, 4045, 4055, 4077 in combination each with 25 parts by weight of Super Sta-tac, Betaprene Nevtac, Escorez, Hercotac, Wingtack, Piccotac, polyterpene, Zonarez, Nirez, Piccolyte, Sylvatac, glycerol ester of rosin (Foral), pentaerythritol ester of rosin (Pentalyn), saturated alicyclic hydrocarbon (Arkon P), coumarone indene (Cumar LX), hydrocarbon (Picco 6000, Regalrez), mixed olefin (Wingtack), alkylated aromatic hydrocarbon (Nevchem), Polyalphamethylstyrene/vinyl toluene copolymer (Piccotex), polystyrene (Kristalex, Piccolastic), special resin (LX-1035) and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXXIII

Gels of 100 parts of Septon (SEEPS) copolymers 4033, 4045, 4055, 4077 in combination each with 25 parts by weight of Super Sta-tac, Betaprene Nevtac, Escorez, Hercotac, Wingtack, Piccotac, polyterpene, Zonarez, Nirez, Piccolyte, Sylvatac, glycerol ester of rosin (Foral), pentaerythritol ester of rosin (Pentalyn), saturated alicyclic hydrocarbon (Arkon P), coumarone indene (Cumar LX), hydrocarbon (Picco 6000, Regalrez), mixed olefin (Wingtack), alkylated aromatic hydrocarbon (Nevchem), Polyalphamethylstyrene/vinyl toluene copolymer (Piccotex), polystyrene (Kristalex, Piccolastic), special resin (LX-1035) and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40oC of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE XXXIV

A 15 layer rolled/folded crystal gel film actuator having a active muscle length of 10 mm and a diameter of 3 mm (made from 0.5 mm thick Septon 4055, 4077, 4045 SEEPS having a 500, 600, 700, 800, 1200, 1600, 1800, 2000, 2300, 2500 gram Bloom gel) is found to have a stroke and a force greater than actuators made from amorphous SEPS, SEBS gels.

EXAMPLE XXXV

A 15 layer rolled/folded crystal gel film actuator having a active muscle length of 10 mm and a diameter of 3 mm (made from 0.5 mm thick Ethylene-styrene copolymers: ES16, ES24, ES27, ES28, ES28, and ES30 having a 500, 600, 700, 800, 1200, 1600, 1800, 2000, 2300, 2500 gram Bloom gel) is found to have a stroke and a force greater than actuators made from amorphous SEPS, SEBS gels.

EXAMPLE XXXVI

A 15 layer rolled/folded crystal gel film actuator having a active muscle length of 10 mm and a diameter of 3 mm (made from 0.5 mm thick made from a 50% of Ethylene-styrene copolymers: ES16, ES24, ES27, ES28, ES28, ES30 with a 50% of Septon 4055 having a 500, 600, 700, 800, 1200, 1600, 1800, 2000, 2300, 2500 gram Bloom gel) is found to have a stroke and a force greater than actuators made from amorphous SEPS, SEBS gels.

While preferred components and formulation ranges have been disclosed herein persons of skill in the art can extend these ranges using appropriate material according to the principles discussed herein. Furthermore, Crystalline midblock segment block polymers can be use in blending with other engineering plastics and elastomeric polymers to make alloyed compositions having improved impact and tear resistance properties. All such variations and deviations which rely on the teachings through which the present invention has advanced the art are considered to be within the spirit and scope of the present invention.